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INFLUENCE OF THE REPLACED ROCK ON REPLACEMENT MINERALS ASSOCIATED WITH ORE DEPOSITS.[1]

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SUMMARY.

In the first part of this paper are considered the possibility of carrying Bowen's reaction series of minerals in igneous rocks into ore solutions and the probability that ore solutions react on wall rocks essentially as magmas react with earlier formed minerals and with foreign rock inclusions. It is concluded that minerals forming in earlier stages of alteration are controlled largely by the mineral composition of the wall rock. Rocks rich in ferromagnesian minerals, like gabbro, yield minerals somewhat lower in the reaction series but still basic. Granite yields minerals much lower in the reaction series than those derived from gabbro. The minerals that form in the advanced stages of alteration are largely controlled by the composition of the solution, regardless of the composition of the wall rock, and all pre-existing minerals are subject to replacement by those that the solution tends to deposit.

[1] Published by permission of the Director of the United States Geological Survey and the Colorado Mining Association.

This paper as first prepared was presented at the Toronto meeting of the Society of Economic Geologists, December, 1930, and submitted to several of the writer's colleagues for criticism. All the critics recognized the difficulty of attempting to extend Bowen's reaction series from the magma to the ore deposit. Some consider that there is a distinct break between the magma and ore solutions and that therefore such an extension can not be made. After considering the criticisms, the writer believes that the idea is worth the attention of geologists, especially as it applies to wall-rock alteration. He has modified the article to meet some of the criticisms, but he has not met and at present can not meet all the criticisms and objections.

In the second part of the paper different deposits are examined to see if the alteration has taken place as expected. The writer concludes that in the main it has. The alteration of sedimentary rocks is believed to be in harmony with the general scheme.

The temperature range of the minerals high in the reaction series is believed to be less than that of the minerals lower in the series. Minerals relatively low in the series may be formed in an advanced stage of high-temperature alteration, but minerals high in the series are never formed at low temperature.

INTRODUCTION.

THE importance of wall-rock alteration associated with the formation of mineral deposits has long been appreciated but especially so since the publication of Lindgren's classic paper on metasomatic processes.[2] Since then Lindgren and many others have added much to our knowledge of the facts and their interpretation. There are still, however, numerous points on which there is not agreement among geologists—for example, the formation of orthoclase (adularia, valencianite). In his earlier paper Lindgren states: "As a product of thermal alteration orthoclase does not commonly appear and has not commonly been recognized until lately. Closer search will probably reveal it in many altered rock and vein fillings of the propylitic type." This type Lindgren would doubtless now include in the epithermal deposits, and his prediction has been amply verified.

In a later work,[3] the same author does not mention orthoclase as a mineral of hypothermal deposits. Adularia is given as "rare" in mesothermal deposits, whereas it is regarded as a common mineral in epithermal deposits in volcanic rocks. He apparently regards orthoclase as forming abundantly in igneous rocks and pegmatites and as largely unstable through hypothermal and mesothermal conditions but forming again under epithermal conditions.

Vogt[4] has pointed out that the lower the content of the albite

[2] Lindgren, Waldemar: Metasomatic processes in fissure veins. Amer. Inst. Min. Eng. Trans., vol. 30, pp. 578–692, 1901.

[3] Lindgren, Waldemar: Mineral Deposits. McGraw-Hill Book Co., 1928.

[4] Vogt, J. H. L.: The physical chemistry of magmatic differentiation of igneous rocks, p. 68, 1926.

molecule the lower the temperature at which orthoclase may form, even to very low temperature. According to Vogt's table, a feldspar of some composition would be stable over a temperature range that would cover most primary ore deposits.

Parker [5] regards vein orthoclase as among the first minerals to form in the Alpine veins and considers it indicative of a relatively high temperature. The present writer has studied a number of deposits in which orthoclase and other minerals have formed at apparently widely different temperatures and has been searching for an explanation of this variation.

Many geologists will doubtless agree that the metal-carrying medium that forms ore deposits is a differentiate from a magma and that, for a large proportion of deposits at least, it is the silicic or alkalic differentiate from an intermediate magma that has passed through the stages that have given rise to diorite, monzonite, granite, pegmatite, and so on, to metal veins. If this is true, the laws governing the differentiation of magmas that result in the formation of igneous rocks of various types should in the main be applicable to the further differentiation product represented by the ore-depositing medium. Also the laws that govern the reactions between later magmatic differentiates and earlier formed rocks and minerals should be applicable to the reaction between the metal-carrying medium and the earlier formed rocks.

Bowen [6] has given a most helpful discussion of the order of mineral formation in the differentiation of a magma and of the result of the reaction between the later magmatic differentiate and the earlier formed minerals and rocks. The accompanying diagram (Fig. 1), gives Bowen's general order of crystallization of the continuous plagioclase series in one line of descent and that of the discontinuous magnesium-iron-aluminum silicate series in another line, with the two merging in the magma that deposits granite.[7] To this diagram the writer has made additions in-

[5] Parker, R. L.: Alpine Minerallagerstätten. Schweiz. Min. u. pet. Mitt., No. 3, p. 298, 1923. Review by Ian Campbell, Amer. Mineral., vol. 12, pp. 157–167, 1927.

[6] Bowen, N. L., The evolution of the igneous rocks, Princeton Univ. Press, 1928.

[7] Bowen, N. L., *op. cit.*, p. 60.

dicated by brackets, and at the suggestion of some of his associates, he has indicated the range of the pyrogenetic, deuteric, and hydrothermal stages.

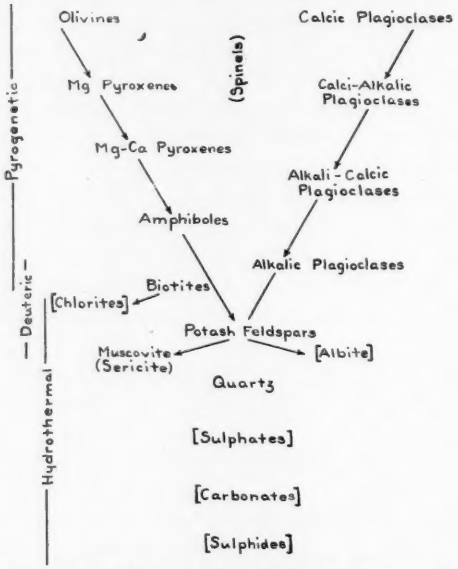

FIG. 1. Order of deposition of minerals from magmas. After Bowen, with groups in brackets added by the writer.

Unfortunately for the students of ore deposits, Bowen has confined his discussion largely to the range above granite, but it is hoped that extension of this discussion may be carried further by someone competent to handle the chemical problems that involve the determination of the phase relations of the minerals that form ore deposits. Meanwhile the geologist may be permitted to go somewhat outside his field to point out some of the helpful features that may result from such a discussion.

Bowen shows that at any stage a magma that is depositing certain minerals will react with earlier formed minerals of any reaction series and that the minerals resulting from these reactions

will be nearer in composition to those that are deposited directly by the magma at that stage; also that when a large amount of magma reacts with a small amount of earlier formed minerals those earlier minerals will be replaced by the same minerals that are being deposited directly. For example, if a magma that is precipitating biotite and oligoclase reacts with a rock composed of olivine and anorthite, the olivine will alter to pyroxene, the pyroxene in turn to amphibole, and the amphibole to biotite. Likewise the anorthite will alter through the series to bytownite and eventually to oligoclase.

If a granitic magma reacts with an olivine-anorthite rock and the reaction does not go to completion a pyroxene-bytownite rock may result. If the same magma reacts on a pyroxene-bytownite rock a biotite-andesine rock may result, and if both reactions go to completion they will give essentially the same end product—namely, the minerals of a granite.

Bowen says:[8]

> It may be stated immediately that any magma will tend to make inclusions over into the phase or phases with which it is saturated, in so far as the composition of the inclusions will permit. It may be stated also that any magma saturated with a certain member of a reaction series is effectively supersaturated with all higher members of that reaction series. It can not, in any sense, dissolve inclusions of such higher members but can only react with them to convert them into that member of the reaction series with which it is saturated, often by passing through other members of the series as intermediate steps. The material used to effect these changes can not be regarded as simply subtracted from the liquid, for the liquid is not free to become impoverished in any random substance. In general, impoverishment in any substance will cause the liquid to pass within a region of saturation and induce the precipitation of some of the phases with which the liquid is saturated.
>
> Let us take, for example, a magma saturated with biotite, say a granitic magma. This magma is effectively supersaturated with olivine, pyroxene, and amphibole, and can not dissolve them in spite of the marked contrast of composition, which is often supposed to be an aid to the solution of inclusions. But the magma can and will react with these minerals and convert them into biotite, usually by steps. The subtraction of material necessary to produce biotite will cause the precipitation of the minerals with which the magma is saturated until either the liquid or the

[8] *Op. cit.*, p. 197.

inclusions are used up or the reaction is brought to an end on account of mechanical obstruction.

Similarly, granitic magma saturated with an acidic plagioclase can not dissolve basic plagioclase but can only react with it and convert it into more acid plagioclase.

There are differences that should be recognized between the reaction series that Bowen has discussed and any reaction series in ore solutions, and with our present knowledge, there are clearly defined limits to the establishment of such series. A fundamental difference is that the magma as discussed by Bowen is essentially a closed system, and its crystallization results from loss of heat, whereas ore deposition is an open system, with the solutions moving in and out, giving renewal of solution and possibly additions or subtractions of heat.

One difficulty is that reaction series can be established only by an understanding of the phase relations. For magmatic minerals some of the phase relations have been experimentally established, and these give a control for geologic deductions. For ore minerals practically no phase relations have been established, and consequently there is no control for geologic deductions with respect to them. As ore deposits are not formed in a closed system there is a possibility that conditions may be reversed and therefore that reactions will not always move in the direction normal to a closed system. With the difficulties and the limitations of the problem kept fully in mind, it yet seems worth while to consider some of the possibilities, especially those pertaining to wall-rock alteration by ore-forming solutions.

We may consider the ore-forming solution or " ore magma " as beginning in the pegmatite stage, where orthoclase or microcline and quartz are precipitating; passing to the deuteric stage, with the precipitation of quartz and replacement of orthoclase or microcline by albite, and on to the hydrothermal stage, with the precipitation of sulphates, carbonates, and sulphides, and perhaps an end product approaching water. If during any of these stages of the solution—say the one depositing quartz—there were reaction with olivine-anorthite rock, a pyroxene-bytownite rock or a

biotite-andesine rock might result, as already suggested. If the same solution were acting on a granite (quartz-orthoclase-biotite rock) a quartz-sericite rock might result. In both types silicification might be the final process.

An ore-forming solution may then, in its simplest form, be regarded as a magmatic differentiate which is brought into contact along fissures with earlier materials of crystallization from the same magma. The composition of the resulting altered rock will depend on the composition of the rock that is altered, the composition of the solution, and the stage to which the reaction progresses.

The same solution acting on different rocks would be expected to yield different minerals in the early stages of the alteration. If it were flowing vigorously along a fissure, the reacting solution would be constantly renewed and the reaction close to the fissure might go essentially to completion, producing minerals that would be precipitated directly from the solution. If a solution were precipitating quartz, its reaction with a wall rock of a ferromagnesian type would result in the early alteration of the calcium and magnesium minerals and the partial or complete removal of calcium and magnesium. The alkali minerals, notably the potash minerals, would be relatively stable during the early stages of alteration, and if the solution contained potash it would combine with the alumina liberated by alteration of calcic feldspars and ferromagnesian minerals to form additional potash minerals. There would therefore be not only a residual concentration but even an actual addition of potash. In the final stages, the potash minerals in turn would be unstable, and there would result a removal of potash, a residual concentration of silica, and possibly also an addition of silica; and the final process would be silicification of any kind of rock. If the solutions were depositing carbonate and sulphide the end products would be carbonates and sulphides, and the silica along with the other elements would be removed.

EXAMPLES OF METASOMATIC ALTERATION.

Let us examine some examples of metasomatic alteration and see to what extent they meet expectation.

Quartz-Diorite, Engels, Cal.—Knopf and Anderson [9] have presented a particularly interesting example of rock alteration in the Engels district, California, where apparently ore-bearing solutions of the same type under essentially the same physical conditions have reacted with rock of quite different composition. Some of the ore bodies are in a hornblende gabbro; others are in quartz diorite. The composition of these rocks and their alteration products are shown in Table I.

TABLE I.

MINERAL COMPOSITION OF FRESH AND ALTERED ROCKS, ENGELS MINE, CAL.

Hornblende Gabbro.

Fresh.	*Altered.*
Bytownite, An_{80} to An_{85}	Andesine, An_{45}
Hornblende (deep brown)	Actinolite
Hypersthene (little)	Biotite
Augite (little)	Chlorite (little)
	Magnetite
	Ilmenite

Quartz Diorite.

Fresh.	*Altered.*
Andesine, An_{35} to An_{45}	Andesine (residual)
Hornblende	Orthoclase
Biotite	Biotite
Orthoclase (little)	Magnetite
Magnetite	Siderite
Apatite	Titanite
Zircon	Zeolite

In the alteration of the gabbro, bytownite has been replaced by andesine; brown hornblende, hypersthene, and augite by actinolite, biotite, and chlorite. In the alteration of quartz diorite, andesine has been largely replaced by orthoclase and hornblende and biotite have altered to biotite. This is essentially the difference that is to be expected if a solution of the same composition were reacting with the different rocks.

[9] Knopf, Adolph, and Anderson, C. A.: The Engels copper deposits, California. ECON. GEOL., vol. 25, pp. 14–35, 1930.

Amphibolite, Southeastern Alaska.—A somewhat similar change in which an amphibolite has altered to a rock rich in

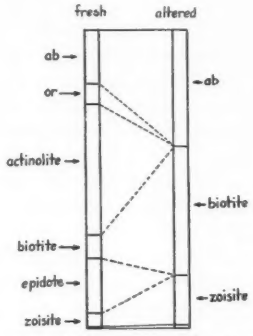

FIG. 2. Alteration of amphibole near Mendenhall Glacier, Alaska.

biotite has also been noted by Knopf from Alaska. The change in alteration is shown in Table II., and in Fig. 2.

TABLE II.

COMPOSITION OF FRESH AND ALTERED AMPHIBOLITE NEAR MENDENHALL GLACIER, SOUTHEASTERN ALASKA.[10]

	Fresh.	*Altered.*
Orthoclase (mol.)	6.7	...
Albite (mol.)	18.3	39.3
Actinolite	43.7	...
Biotite	7.9	43.1
Zoisite	4.5	16.4
Epidote	18.3	...
Apatite	0.6	1.2

The rocks of southeastern Alaska are rich in soda and poor in potash, and replacement by albite rather than by the potash minerals is characteristic.

Alaska-Treadwell Mine.—Spencer[11] describes metasomatic alteration in the Alaska-Treadwell mine as follows:

[10] Knopf, Adolph, in Lindgren, Waldemar: Mineral deposits, 3d ed., p. 759, 1928.

[11] Spencer, A. C.: The Juneau Gold Belt. U. S. Geol. Survey Bull. 287, p. 111, 1906.

The rock characteristically contains two sorts of feldspar—namely, albite-oligoclase and microperthite. The first occurs in phenocrysts of fairly definite form, often showing concentric structure and always clouded by decomposition products, except that they frequently have narrow rims of clear material which are probably secondary. The microperthite, which has the characteristic mottled appearance of this minute intercrystallization of albite and orthoclase, is entirely interstitial as regards the albite-oligoclase. The metasomatic replacement of this interstitial microperthite by albite is the most striking feature presented by the alteration of the rock. In some cases the replacement has gone so far that the crystals of albite-oligoclase have been attacked, as shown by their corroded contacts with the albite mosaic.

Sudbury, Ontario.—Rocks associated with the Sudbury nickel deposits afford an interesting example of alteration that has been described by Wandke and Hoffman,[12] who have pointed out that the alteration corresponds to Bowen's series. Numerous types are described, and one of these descriptions is quoted:

Judging from the minerals now remaining, the original rock was an augite gabbro. The various steps leading to complete granitization are still fairly decipherable. Among these steps are: (1) The breakdown of the large crystals of pyroxene to form a multitude of small crystals of pyroxene, magnetite, biotite, plagioclase, and hornblende (actinolite), and the breakdown of the large crystals of plagioclase into a mosaic of small crystals of plagioclase; (2) the pyroxene is gradually replaced, and the hornblende and the magnetite tend to form larger grains, the plagioclase changes from labradorite to oligoclase and albite; (3) oligoclase and albite increase in amount, although preserving the granular habit, and apatite and quartz begin to become abundant; (4) with the advent of quartz the hornblende begins to disappear; (5) the end result is a rock consisting essentially of albite, oligoclase, hornblende, a little biotite, with apatite and magnetite as accessories. The development of the sulphides and associated minerals follows the above-mentioned steps. . . . With the advent of the sulphides the albite and oligoclase formed during the period of granitization of the greenstone become cloudy with chlorite, epidote, zoisite, calcite, and sericite. Even the apatite alters to epidote. In the basic rock magnetite has been largely replaced by green chlorite, epidote, and titanite. The hornblende formed during the period of granitization altered to chlorite, carbonate, quartz, and epidote. The biotite of the same period changed to chlorite and rutile.

[12] Wandke, Alfred, and Hoffman, Robert: A study of Sudbury ore deposits. ECON. GEOL., vol. 19, pp. 169–204, 1924.

Monzonite Porphyry, Ely, Nevada.—Spencer [13] has given a most instructive description of the alteration of monzonite porphyry at Ely, Nevada, in which the original minerals have been replaced by those lower in the magmatic series. He says:

The alterations of the porphyry which are of the greatest interest to the formation of copper ores of the disseminated type are those which have been produced through the permeation of the rock mass by magmatic solutions. These alterations comprise, in different stages, the progressive destruction of hornblende, of plagioclase, and of magnetite, and the formation in their stead of mica, including the white variety of felty habit commonly called sericite and a brown variety allied to biotite; the deposition of pyrite and chalcopyrite, and of calcite. Titanite is decomposed and titanic oxide separated, but apatite commonly survives unaltered. Orthoclase phenocrysts are commonly not attacked, though under very strong alteration they change into sericite or break up into small grains. The orthoclase of the normal groundmass and the quartz which accompanies it have been dissolved and redeposited as an aggregate of finer grain, commonly with the addition of brown mica and

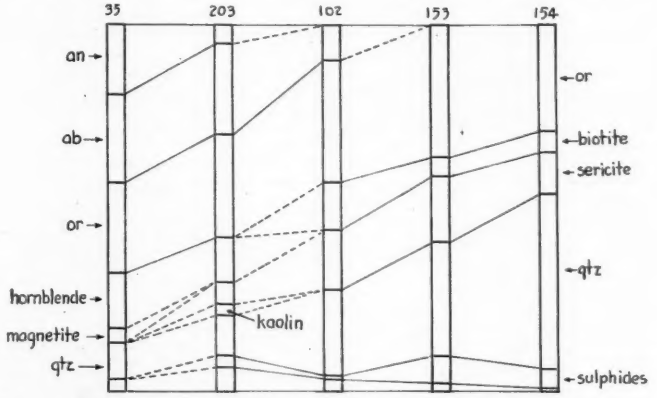

FIG. 3. Mineral composition of normal and metamorphosed porphyry, Ely Quadrangle, Nevada.

characteristically with the addition of distributed grains of pyrite and chalcopyrite. Thus the groundmass of thoroughly altered porphyry has

[13] Spencer, A. C.: The geology and ore deposits of Ely, Nevada. U. S. Geol. Survey, Prof. Paper 96, p. 56, 1917.

a granulated appearance quite distinct from that of the normal rock. The quartz grains of the re-formed matrix commonly contain cavities partly filled with a fluid. Where the rock is extremely altered the primary phenocrysts of orthoclase and the orthoclase of the secondarily crystallized groundmass have been replaced by sericite, and the biotite has been bleached so that the final product of alteration is a felt of sericite flecked with grains of sulphide and of quartz. Pyrite and chalcopyrite occur mainly in the altered groundmass but are also found in the sericite aggregates and rarely ever in the large orthoclase crystals.

Alterations of the kind described have involved the more or less complete abstraction of lime and soda and the partial elimination of magnesia, iron, and alumina. Hand in hand with these losses there has been a marked gain in potash, in sulphur, and in water of constitution.

Table III. shows the mineral changes in the alteration of the rock, and this is shown diagrammatically in Fig. 3.

TABLE III.

MINERAL COMPOSITION OF NORMAL AND METAMORPHOSED PORPHYRY, FROM ELY, NEVADA.[14]

	35	203	102	153	154
Quartz	10.00	11.00	23.30	31.00	48.00
Orthoclase	24.50	28.00	33.60	36.00	29.00
Albite	24.00	25.00	9.40	....	....
Anorthite	19.20	5.00	.00	....	....
Hornblende	15.00	[a]12.00	....	....	....
Apatite	.51	1.00	1.00	....	....
Sphene	1.76	1.70	....	....	....
Magnetite	4.00	....	....	....	....
Biotite	....	....	13.00	5.00	5.90
Sericite	....	6.00	16.00	18.00	11.00
Kaolin	....	3.00	....	....	....
Calcite and fluorite	.15	1.70	1.3	....	....
Pyrite	.13	3.10	.30	[b]3.83	2.22
Chalcopyrite	....	.20	1.00	1.83	1.63
Chalcocite	....	....	....	1.66	1.25
	99.25	98.70	99.00	97.32	99.00

35, Monzonite porphyry. 203, Partly metamorphosed porphyry. 102, Ore porphyry. 153, Porphyry ore. 154, Siliceous variety of porphyry.

a Hornblende, chlorite, epidote, and biotite. *b* FeS = 3.18; Fe_2S_3 = 0.65.

Monzonite, Bingham, Utah.—The disseminated deposits of the

[14] Spencer, A. C.: U. S. Geol. Survey, Prof. Paper 96, p. 58.

Bingham district, Utah, are very similar to those of Ely. They have been described by Butler [15] as follows:

In the Bingham district the earlier stages of alteration of the monzonite resulted in the transformation of the hornblende and augite into biotite, in partial sericitization of the feldspars, and in the transformation of much of the groundmass of the rock into a fine-grained aggregate of quartz and orthoclase. The altered rock is known as dark porphyry. Pyrite and chalcopyrite are scattered through the rock. Where the alteration has been more intense the rock has been largely converted into a fine-grained aggregate of quartz and orthoclase, some sericite, and small disseminated grains of pyrite and chalcopyrite. This is known as 'light porphyry.'

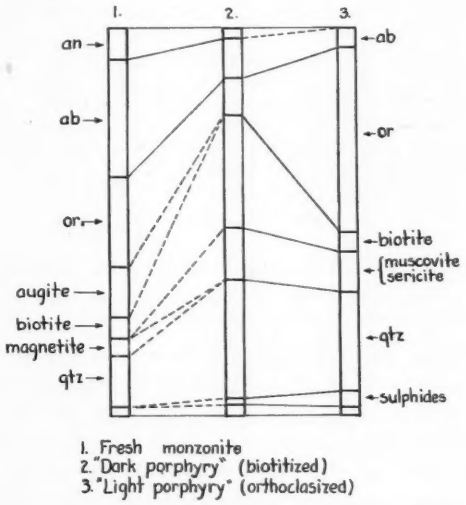

FIG. 4. Alteration of monzonite wall-rock adjacent to fissures, Bingham district, Utah.

Table IV. and Fig. 4 show the mineral changes that have resulted from the alteration:

[15] Butler, B. S., and others: Ore deposits of Utah. U. S. Geol. Survey Prof. Paper 111, p. 161, 1920.

TABLE IV.

MINERAL COMPOSITION OF FRESH AND ALTERED MONZONITE, BINGHAM DISTRICT, UTAH.[16]

	1	2	3
Quartz	13.20	30.54	25.26
Orthoclase molecule	23.25	9.45	47.82
Albite molecule	30.39	9.96	4.19
Anorthite molecule	8.06	2.78	.83
Augite	12.70	....	....
Biotite	5.50	29.19	5.05
Magnetite	4.41	....	....
Sphene	.78	....	....
Muscovite molecule	6.37	13.24	10.35
Paragonite molecule	6.87		
Rutile	....	.43	.47
Apatite	....	1.01	.34
Calcite	....	....	....
CuS	....	.35	.45
$CuFeS_2$	....	.47	2.84
FeS_2	....	.83	.95
H_2O	1.50	2.09	1.26

1. British tunnel, Last Chance mine, Bingham district; fresh rock.

2. Boston Consolidated mine, Sub. 8, No. 31, crosscut north of drift No. 6; altered rock, "dark porphyry."

3. North end of Pit-Utah copper mine; altered rock, "light porphyry."

The early increase in the micas and the later decrease, with increase in orthoclase, is the notable feature of the alteration at Bingham.

Silver Plume Granite, Climax, Colorado.—The Climax molybdenum deposits of Colorado constitute an interesting example that was recently studied by the writer and John W. Vanderwilt[17] and gave rise to the present review of rock alteration. The alteration of the pre-Cambrian Silver Plume granite and the Tertiary quartz monzonite porphyry dikes is in many ways similar to the alteration in the Bingham and Ely districts. The earliest alteration is that of the phenocrysts of plagioclase, which become strongly sericitized. In this stage the orthoclase seems to be little affected. At about the same time, the dark silicates are replaced by secondary biotite. Next the groundmass recrystallizes

[16] Butler, B. S., et al. *op. cit.*, p. 166.

[17] Butler, B. S., and Vanderwilt, J. W.: The Climax molybdenum deposits. Colorado Sci. Soc. Proc., vol. 12, pp. 309–353, 1931.

to a mosaic of secondary quartz and orthoclase, and this material begins to replace the orthoclase phenocrysts. Eventually it may partly or wholly replace the sericitized plagioclase phenocrysts, and the rock becomes essentially a quartz-orthoclase rock with some sericite. The next stage is the addition of quartz at the expense of feldspar until the highly altered rock is largely quartz, containing small amounts of pyrite.

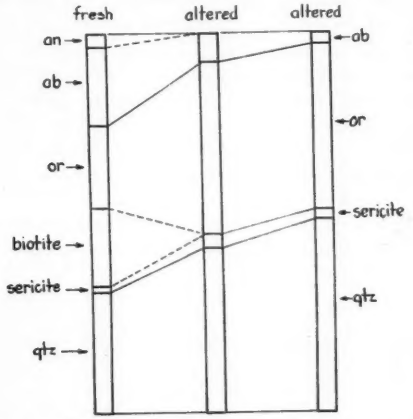

FIG. 5. Mineral changes in alteration of Silver Plume granite, Climax, Colorado.

Table V. and Fig. 5 show the mineral changes that took place in the granite during alteration. No analysis of the stage of intense silicification is available, but it would show little except SiO_2.

TABLE V.

MINERAL CHANGES IN ALTERATION OF SILVER PLUME GRANITE, CLIMAX, COLORADO.

	Fresh.		Altered.	
Quartz		31.63	42.81	49.50
Orthoclase		21.86	46.11	44.31
Albite	20.68	22.92	6.70	2.32
Anorthite	2.24			
Muscovite (sericite)		.95	2.79	1.53
Biotite		20.77	....	....
Magnetite		.51	....	....

Quartz monzonite porphyry, Morenci, Arizona.—Lindgren [18] has described the alteration of a quartz monzonite porphyry from Morenci, Arizona, consisting mainly of plagioclase, orthoclase, and quartz as follows:

The sericitized rock becomes bleached, dull white, and chalky; the feldspar prisms lose their luster; albite and oligoclase, as well as orthoclase, become filled with sericite foils, at first oriented parallel to the cleavage, and later completely pseudomorphed by a sericite felt mixed with occasional quartz grains. No epidote nor chlorite develop in the feldspars. The quartz phenocrysts remain unaltered. The biotite first becomes converted to chlorite and sericite and is sometimes also pseudomorphed to the latter mineral. In wholly altered rocks the chlorite is transformed to irregularly spreading serpentine, often difficult of detection. A little epidote is occasionally present. Kaolin and chalcedonic quartz are found in places, but are connected with a later process of chalcocitization.

In the groundmass of the porphyry the feldspars are transformed into an aggregate of sericite, the quartz grains remaining unaltered. Finally pyrite forms more or less abundantly.

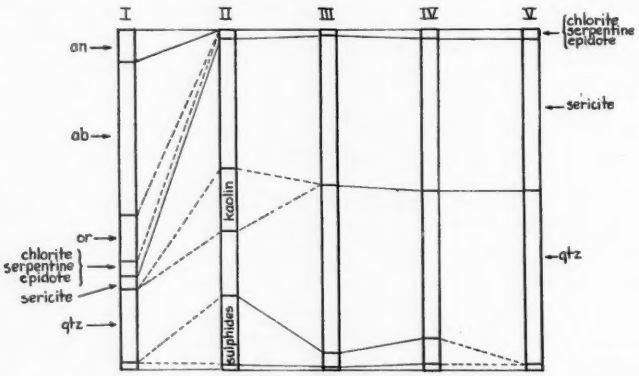

FIG. 6. Mineral contents of fresh and altered quartz-monzonite porphyry, Clifton-Morenci district, Arizona.

Table VI. and Fig. 6 show the mineral changes:

[18] Lindgren, Waldemar: The copper deposits of the Clifton-Morenci district, Ariz. U. S. Geol. Survey Prof. Paper 43, pp. 165–166, 1905.

TABLE VI.

MINERAL CONTENTS OF FRESH AND ALTERED QUARTZ MONZONITE PORPHYRIES, CLIFTON-MORENCI DISTRICT, ARIZONA.[19]

	I.	II.	III.	IV.	V.
Quartz	21.35	19.13	49.33	43.03	50.81
Orthoclase (mol.)	13.12	.....	.....	.....	.....
Albite (mol.)	45.26	.....	.....	.....	.....
Anorthite (mol.)	9.52	.....	.....	.....	.....
Apatite	.28	.36	.12	.30	.12
Zircon	.02	.....	.....	.....	.....
Magnetite	.41	.....	.....	.....	.....
Ilmenite	.81	.....	.....	.....	.....
Rutile	.....	.43	.41	.38	.45
Sericite	3.75	38.50	43.44	44.94	44.29
Kaolin	.....	17.90	.....	.....	.....
Chlorite	3.04	.....	.....	.....	.....
Serpentine	.98	2.81	1.71	2.74	2.71
Epidote	.59	.....	.43	.....	.36
Alunite	.....	.46(?)	.26(?)	.26(?)	.21(?)
Water (below 100° C.)	.60	.94	1.00	.83	1.21
FeS_2	.24	19.18	3.09	4.96	.06
Cu_2S	.02	.24	.07	2.42	.....
ZnS	.03	.32	.....	.....	.....
MoS_2	.....	.20	.....	.....	.....
	100.02	100.47	99.86	99.86	100.22

I., Fresh monzonite porphyry. II., Altered monzonite porphyry. III., Altered (silicified) porphyry. IV., Altered porphyry within chalcocite zone. V., Altered porphyry.

It is clear that in this rock also, the alteration products are minerals lower in the series.

Dacite, Goldfield, Nevada.—Without multiplying examples, we may pass to a rather extreme type,—the alteration of dacite at Goldfield, Nevada, as described by Ransome:[20]

The altered rock is light gray, flecked with numerous dull-white spots which represent the original feldspar phenocrysts. The few quartz phenocrysts are unchanged, but the ferromagnesian, or, more briefly, femic, minerals have wholly disappeared.

Under the microscope it is seen that the only original constituents are the quartz phenocrysts; even these show some development of pyrite along irregular microscopic cracks, and an occasional small crystal of zircon. The feldspars are changed to aggregates of minutely crystalline kaolinite and tabular crystals of alunite. . . .

Quartz also accompanies the alunite and kaolinite in some of the

[19] Lindgren, Waldemar: *op. cit.*, p. 169.

[20] Ransome, F. L.: Geology and ore deposits of Goldfield, Nevada. U. S. Geol. Survey Prof. Paper 66, p. 179, 1909.

pseudomorphs after labradorite. Diaspore, while not present in the rock analyzed, occurs in the alunitized dacite in the Florence mine and elsewhere. The former femic constituents can be recognized from the fact that they contain little or no kaolinite, the quartz and alunite here being associated with pyrite.

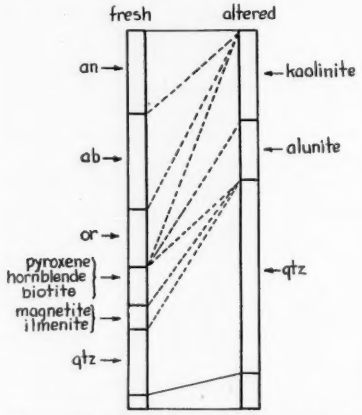

FIG. 7. Mineral composition of fresh and altered dacite from Goldfield, Nevada.

Table VII. and Fig. 7 show the mineral changes that have taken place in the alteration of the dacite.

TABLE VII

MINERAL COMPOSITION OF FRESH AND ALTERED DACITE FROM GOLDFIELD, NEVADA.[20]

		Fresh (norm.)	Altered
Quartz		17.34	49.38
Orthoclase		15.01	....
Albite	25.68	47.64	....
Anorthite	21.96		
Diaspore		5.21	....
Enstatite		4.63	....
Magnetite		4.87	....
Ilmenite		1.52	....
Apatite		.34	....
Zircon		.37	....
Kaolinite			23.99
Alunite			15.73
Pyrite			7.20
Water			2.53
Other constituents			1.17

Here the solutions that are depositing sulphate are apparently out of the range of those that deposit common rock-forming minerals except quartz and, with this exception, all the rock-forming minerals are altered and none are deposited.

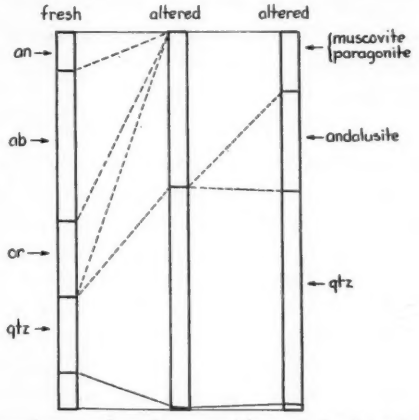

FIG. 8. Approximate mineral composition of fresh and altered latite, San Francisco district, Utah.

Latite, San Francisco district, Utah.—Another rather extreme type of metasomatic replacement has been described by Butler,[21] in which the abundant sericite of the intermediate stage of altera-

TABLE VIII.

MINERAL COMPOSITION OF FRESH AND ALTERED LATITE, SAN FRANCISCO DISTRICT, UTAH.

	Little altered	Moderately altered	Highly altered
Quartz	20	58.0	56.34
Orthoclase molecule	20	....	.....
Albite molecule	40	....	.....
Anorthite molecule	10	....	.....
Muscovite molecule	..	34.2	7.96
Paragonite molecule	..	6.7	7.64
Andalusite	..	....	26.35
Ilmenite	..	....	1.05
Rutile	..	....	.55
Calcite	..	.6	.....

[21] Butler, B. S.: U. S. Geol. Survey Prof. Paper 80, p. 79, 1913.

tion gives place in the more advanced stage to aluminum silicate, andalusite. The change is shown in Table VIII. and Fig. 8.

In this type of alteration there has clearly been progressive leaching of bases in excess of alumina. Where potash was not present in the amount necessary to combine with alumina for muscovite, the aluminum silicate andalusite formed. Why the anhydrous silicate formed is not known, but it may have been due to high temperature.

GENERAL DISCUSSION.

From the examples cited it seems evident that in many rocks where metasomatic replacement has occurred the alteration has followed the line of descent that would be expected. In some rocks, however, notably those whose final products are low in the series, the intermediate steps are poorly represented or lacking. Examples of such alteration are the sericitization of quartz monzonite at Morenci and the kaolinization and alunitization of dacite at Goldfield. The early alteration product of plagioclase, moreover, is commonly sericite, even where orthoclasization is the dominant alteration and where the sericite may later give place in part to orthoclase. As a possible control of the potash mineral that will form or the proportions of the different potash minerals that form we may consider the composition of the minerals as shown in Table IX.

The ratio of K_2O to Al_2O_3 is highest in orthoclase and phlogopite, lowest in muscovite and alunite, and intermediate in biotite.

The ratio of K_2O to SiO_2 is the same in all the potassium silicates. The ratio of Al_2O_3 to SiO_2 is greatest in muscovite and least in orthoclase. Which of these ratios is likely to be of the greatest significance in determining which minerals shall form? In most of the rocks studied there appears to have been an excess of silica, so that it was available for the formation of any of the minerals, though its abundance may have been a factor in determining the mineral to form.

It seems very likely that K_2O was not invariably present in sufficient quantity to combine with all the Al_2O_3 to form orthoclase, and if it was not, instead of forming orthoclase and aluminum

oxide or aluminum silicate, the K_2O combined in less ratio with the Al_2O_3 to form mica or both mica and orthoclase as the proportions of K_2O and Al_2O_3 permitted.

TABLE IX.

MOLECULAR RATIOS OF CONSTITUENTS OF SOME POTASSIUM MINERALS AND THE PLAGIOCLASE FELDSPARS.

Orthoclase, $KAlSi_3O_8$	$K_2O : Al_2O_3 :: 1 : 1$ $K_2O : SiO_2 :: 1 : 6$ $Al_2O_3 : SiO_2 :: 1 : 6$
Muscovite, $Al_3KH_2Si_3O_{12}$	$K_2O : Al_2O_3 :: 1 : 3$ $K_2O : SiO_2 :: 1 : 6$ $Al_2O_3 : SiO_2 :: 1 : 2$
Biotite, $Al_2Mg_2KHSi_3O_{12}$	$K_2O : Al_2O :: 1 : 2$ $K_2O : SiO_2 :: 1 : 6$ $Al_2O_3 : SiO_2 :: 1 : 3$
Phlogopite, $AlMg_3KH_2Si_3O_{12}$	$K_2O : Al_2O_3 :: 1 : 1$ $K_2O : SiO_2 :: 1 : 6$ $Al_2O_3 : SiO_2 :: 1 : 6$
Alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$	$K_2O : Al_2O_3 :: 1 : 3$
Albite, $NaAlSi_3O_8$	$Na_2O : Al_2O_3 :: 1 : 1$ $Na_2O : SiO_2 :: 1 : 6$ $Al_2O_3 : SiO_2 :: 1 : 6$
Anorthite, $CaAl_2Si_2O_8$	$CaO : Al_2O_3 :: 1 : 1$ $CaO : SiO_2 :: 1 : 2$ $Al_2O_3 : SiO_2 :: 1 : 2$

When plagioclase feldspars break down, early in the metasomatic process, there is probably not enough K_2O immediately available within the area occupied by the plagioclase to combine with the freed Al_2O_3 to form orthoclase, so muscovite is formed. On the other hand, if orthoclase recrystallizes to another orthoclase, of slightly different composition, the ratio for orthoclase is maintained. Likewise, if the altering solutions are poor in K_2O, sericite would be expected to form; if rich in K_2O, orthoclase might form even as a replacement of plagioclase.

In the formation of orthoclase and sericite, therefore, the composition of both the rock and the altering solutions would seem to

be controlling factors. If so, both might be expected to form over a wide temperature range or to be " persistent " minerals, and their occurrence seems to verify such expectation.

It has been repeatedly pointed out by different workers that the plagioclase feldspars and the rock-forming ferromagnesian minerals are unstable in the presence of vein-forming solutions and that in the early stages of alteration there is a removal of a large proportion of the calcium, magnesium, and sodium, although under some conditions sodium and more rarely calcium and magnesium are not leached. The aluminum freed by the breakdown of these minerals combines in part with potassium, either that present in the rock or that in the solutions. There results a residual concentration of potassium and aluminum as well as silica and in some rocks an actual addition of potassium from the altering solutions. In the early stages of alteration, then, potassium, aluminum, and silica tend to concentrate in the altered rock. The solutions, on the other hand, tend to become richer in calcium, magnesium, and sodium from the altered rock. In due course the solutions may become sufficiently rich in those elements to deposit them. This may account for veins of calcium and magnesium carbonate or the addition of compounds of these elements in the wall rocks.

If alteration of the potassium-rich rock continues, both potassium and aluminum are eventually leached. In some rocks apparently they are leached in the proportion in which they are present; in other rocks the potassium is leached more rapidly and aluminum silicate or oxides are formed. In this later stage of alteration, which results in silicification, the solutions again become richer in potassium and aluminum, which farther on in their journey may be again precipitated as adularia, perhaps replacing the calcium and magnesium that have preceded them and again driving these elements forward.

The whole trend of the process is toward leaching of the bases and silicification, but during the process there is separation of the bases and in places temporary concentration of certain of them.

The discussion thus far has been confined mainly to solutions

that precipitate quartz or minerals higher in the series. If the solutions are such as tend to precipitate minerals below quartz in the series, as carbonate or sulphide, quartz will not be stable and will be replaced. Numerous examples might be cited of quartz replaced by carbonates and sulphides—in fact, such replacement is characteristic of the later stages of mineralization in veins.

REPLACEMENT OF SEDIMENTARY ROCKS.

Sedimentary rocks represent the separation and segregation of the elements of igneous rocks. Their alteration presents special forms in the reaction series, but not fundamentally different from those of igneous rocks. In the main the minerals are different from those in the igneous rocks. Lime and magnesia are segregated in the limestones and dolomites, quartz in the sandstones, and aluminum in the shales. The reactions are, however, those that would be expected from the consideration of the alteration of igneous rocks. If the dolomites and limestones are compared with the basic igneous rocks rich in magnesium and calcium the resulting products are not so different except for the aluminum content. At the other extreme sandstone if acted on by a solution depositing minerals above quartz will probably be sericitized, and if acted on by a solution depositing minerals below quartz it will be replaced.

INFLUENCE OF TEMPERATURE.

In the preceding paragraphs temperature has not been considered. However, it is not the intention to imply that temperature is not a factor in determining what minerals shall form or to question the validity of classifying deposits on the basis of temperature of formation.

If olivine, for example, reacts with an ore solution at high temperature, pyroxene and magnetite will probably be the first products to form, although they in turn may be changed to other minerals, even as low in the series as chlorite. If similar solutions at low temperature react with olivine, doubtless a hydrous ferro-magnesian mineral, chlorite or serpentine, would result directly.

In other words, high-temperature conditions in advanced stages of alteration may produce minerals low in the magmatic series. Low-temperature conditions will produce only minerals low in the magmatic series, never those high in the series. The minerals high in the magmatic series therefore seem to have a more restricted temperature range than those lower in the series and therefore to be more diagnostic of temperature conditions.

ACKNOWLEDGMENTS.

No attempt has been made in this paper to review the great volume of literature on rock alteration. A few examples have been chosen that seem to illustrate the points in mind.

The writer wishes to acknowledge the helpful discussions of the problems with his colleagues of the United States Geological Survey, especially those engaged in the Colorado coöperative work and Messrs. G. F. Loughlin and C. S. Ross, and also with his associates at the University of Arizona.

I am indebted to Mr. Chas. H. Johnson, of the Arizona Station of the United States Bureau of Mines, for assistance in the preparation of illustrations.

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TEMPERATURE OF FORMATION OF THE ILMENITE OF THE ENGELS COPPER DEPOSITS—A DISCUSSION.

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THE Geological Society of Washington was fortunate in having Professor Knopf present a paper on the Engels copper deposits at one of the meetings last winter. In the discussion which followed I made a few remarks on the argument used to fix the temperature at which the deposit was formed. Since that time I have been urged by several geologists to publish them. Professor Knopf's argument was essentially that used by Knopf and Anderson in their paper on these deposits published in this Journal about a year before.[1] I have accordingly written my remarks as a discussion of that paper. To this I have appended a brief description of a diagram showing equilibrium in a hypothetical binary system, which may be of service in connection with my discussion.

The argument by which Knopf and Anderson arrive at the temperature at which the deposit was formed is so simply and clearly stated in their paper that to attempt to synopsize it would detract from its clarity. I am therefore quoting it in full although I shall discuss only that part by which they seek to fix a lower limit to the temperature.

> Under reflected polarized light the magnetite, ilmenite, chalcopyrite, and bornite, show 'mutual boundaries,' indicating that these minerals were deposited essentially contemporaneously. In places the magnetite and ilmenite are slightly older than the sulphides. The two iron-ore minerals are readily distinguishable in polarized light, the magnetite being isotropic and the ilmenite being anisotropic and showing polysynthetic twinning lamellæ. Under high-power oil-immersion lens the magnetite shows few or no exsolved lamellæ of ilmenite. The ilmenite shows minute discs or lamellæ of hematite that within each grain of ilmenite are arranged

[1] Knopf, Adolph and Anderson, C. A.: The Engels Copper Deposits, California, ECON. GEOL., vol. 25, pp. 14–35, 1930.

as dashed lines in single orientation. These hematite lamellæ were first noticed by Graton and McLaughlin.[2] They are now interpreted as the results of the breakup of an originally homogeneous solution of hematite in ilmenite. The relations of the ilmenite and magnetite allow us, as the result of the important work by Ramdohr [3] and Lindley,[4] to determine the temperature of ore deposition at Engels.

Between 600° and 700°, magnetite, as shown by the experimental homogenization of unmixed solid solutions of magnetite and ilmenite by Ramdohr, is capable of holding considerable ilmenite in solid solution; on slow cooling this ilmenite separates out as narrow lamellæ parallel to the octahedral faces of the magnetite. Inasmuch as the magnetite and ilmenite were deposited contemporaneously at Engels and the magnetite shows no exsolved lamellæ of ilmenite, it follows that the temperature of deposition was below that at which magnetite-ilmenite solid solutions begin to unmix, *i.e.*, between 600° and 700°. The ilmenite-hematite solid solution, which according to Ramdohr appears to unmix with more difficulty than the magnetite-ilmenite solid solution, has in fact unmixed, indicating that the rate of cooling in the Engels ores was slow enough for the magnetite-ilmenite solid solution to unmix, had it existed at Engels, and therefore that the homogeneity of the magnetite is not due to quenching. The ilmenite gives some indication of having unmixed in two generations, the hematite lamellæ of the second generation being practically at the limit of visibility. This occurrence of exsolved hematite in two generations would indicate that the temperatures of deposition of the ilmenite had been above 675°.[5] Thus the upper and lower temperature limits are indicated, and point to a temperature of about 700°.[6]

In this discussion I shall confine my attention to that part of Knopf and Anderson's arguments by which they arrive at a temperature above which the deposit must have formed. No opinion whatever is expressed or implied about the other parts of their argument.

In the sentence "This occurrence of exsolved hematite in two generations would indicate that the temperatures of deposition of the ilmenite had been above 675°" (see above), they base their

[2] Econ. Geol., vol. 12, p. 11, 1917.

[3] Ramdohr, P.: Beobachtungen an Magnetit, Ilmenit, Eisenglanz und Ueberlegungen über das System FeO, Fe_2O_3, TiO_2. *Neues Jahrb. Min.*, Beil. Bd. 54–A, pp. 320–379, 1926.

[4] Lindley, H. W.: Mikrographie der Eisenerzmineralien oberhessischer Basalte. *Neues Jahrb. Min.*, Beil. Bd. 53–A, pp. 323–360, 1925.

[5] Ramdohr, P.: *op. cit.*, p. 375.

[6] Knopf and Anderson: *op. cit.*, pp. 27–29.

argument squarely on Ramdohr's paper. Let us see what evidence for their statement can be derived from Ramdohr's paper. In an earlier paper Ramdohr [7] explained the rather frequent occurrence of two distinct sizes of gashes, discs, or lamellæ in ilmenite, with fine gashes of ilmenite in the coarser hematite, in the following way. At higher temperatures Fe_2O_3 and $FeTiO_3$ are isomorphous and completely miscible in the solid state. At lower temperatures, however, they are only partially miscible,[8] as indicated in Fig. 1.[9] At a still lower temperature the ilmenite

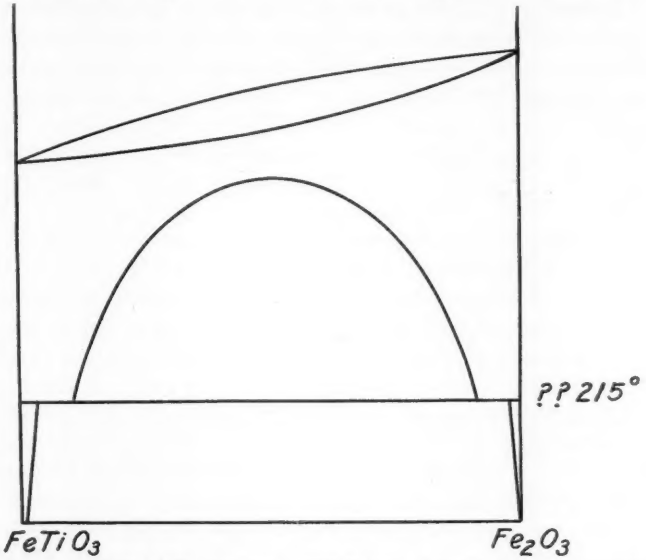

FIG. 1. Ramdohr's proposed equilibrium diagram for the system, $FeTiO_3$–Fe_2O_3 (Ramdohr, P.: *op. cit.*, p. 24, 1924; *op. cit.*, p. 350, 1926). A similar diagram, but without any temperature for the inversions, is given in the summary of the 1926 paper.

[7] Ramdohr, Paul: Beobachtungen an Opaken Erzen. Archiv für Lagerstättenforschung von Preuss. Geol. Landesanstalt, 34, 1924.

[8] For a theoretical discussion of the possible types of binary systems with solid solutions and inversions, see Bakhuis Roozeboom, H. W.: Zeit. phys. Chem., 30, pp. 413–429, 1899.

[9] Fig. 1 is reproduced here from Fig. 4 of Ramdohr's 1924 paper and occurs also as Fig. 2 of his 1926 paper.

loses its higher symmetry and becomes tetartohedral. Accordingly at this temperature the solubility of Fe_2O_3 in $FeTiO_3$ and also that of $FeTiO_3$ in Fe_2O_3 is abruptly reduced, and so the unmixing discs of the second generation originate.[10] This argument is repeated in the 1926 paper.[11] In the earlier paper the temperature at which the inversion occurs and at which the second generation commences to grow was tentatively placed at 215°, at which temperature Königsberger and Schilling[12] had reported finding an inversion in ilmenite.

Assuming with Ramdohr that the binary system, $FeTiO_3$–Fe_2O_3, shows complete solid solution at high temperatures with unmixing at lower temperatures as indicated in the upper part of the diagram, Fig. 1 (or Fig. 2), three points require attention here.

If the compound, $FeTiO_3$ (ilmenite), has both high and low temperature forms which can co-exist in equilibrium at some temperature T_1, or in other words, if there is an inversion at a temperature T_1, and if further, as was assumed, the solubility of Fe_2O_3 is less in the low temperature form of $FeTiO_3$ than in the high, it follows that the temperatures, at which the high temperature form of the solid solutions can exist in equilibrium with the low temperature form, decrease as the amount of Fe_2O_3 in the solid solution increases (see appendix). So solid solutions of Fe_2O_3 in $FeTiO_3$ would not invert, with accompanying unmixing, at the temperature T_1, as Ramdohr supposed, but at some lower temperature. How much lowering of the inversion would correspond to a given amount of Fe_2O_3 is not known. Many systems showing this phenomenon have been investigated and in some of

[10] Ramdohr, *op. cit.*, p. 24, 1924.

[11] Ramdohr, *op. cit.*, pp. 350–351, 1926.

[12] Königsberger, J., and Schilling, K.: Ann. d. Phys., 32, pp. 200–205, 1910. These authors reported finding a very sluggish inversion in a specimen of ilmenite from Miask at about 215° by measurements of electrical conductivity. The exact composition of the specimen was not known but it was stated to be a solid solution of Fe_2TiO_5 and Fe_2O_3. This is probably a slip in stating the formula. Warren (Econ. Geol., vol. 13, pp. 421–422, 1918), gives references to a number of analyses of ilmenite from this locality and lists the mean of three by Rammelsberg which indicate that it is a solid solution of Fe_2O_3 in $FeTiO_3$ with a slight excess of TiO_2. The material studied by Warren was microscopically homogeneous.

them small changes in composition are accompanied by very considerable changes in the inversion temperature. In the well-known system, iron-carbon, for example, about 0.5 per cent. of carbon lowers the temperature of an inversion 140°. It is evident, then, that one cannot in general form a reliable estimate of the temperature of an inversion in a naturally occurring solid solution from a determination made on a single member of the solid solution series to which it belongs.

We have considered the way in which the temperature of an assumed inversion in $FeTiO_3$ would be modified by solid solution. The second point requiring attention is the idea that the inversion in ilmenite demands an abrupt drop in the solubility of $FeTiO_3$ in Fe_2O_3, as shown in Fig. 1. There can be no such abrupt change of solubility at one temperature unless it corresponds to a phase change, *i.e.*, an inversion, in the Fe_2O_3 solid solutions. At the temperature at which the saturated solid solution of Fe_2O_3 in $FeTiO_3$ is assumed to invert with unmixing, an equilibrium diagram, consistent with the assumption, would show the *intersection* of the curves representing the compositions of the Fe_2O_3 solid solutions which can exist in equilibrium with the high and low temperature forms of the $FeTiO_3$ solid solutions (Fig. 2). There would not be a horizontal line joining these curves as there is in Fig. 1. An abrupt decrease in solubility of $FeTiO_3$ in Fe_2O_3 does not follow from the assumption of this inversion in ilmenite: such an abrupt decrease in solubility requires the additional assumption of an inversion in Fe_2O_3, the temperature of which is lowered by solid solution of $FeTiO_3$. Any such abrupt changes of solubility would in general take place at different temperatures in the two solid solutions.

The third point to be noted is that the origin of the smaller gashes as a second generation of unmixing due to the material cooling through an inversion was assumed as a reasonable explanation of observed textures and modes of occurrence of natural ilmenites [13] and did not rest on an experimental basis.

In the 1926 paper Ramdohr described three series of experi-

[13] Since such observations cannot of themselves indicate a temperature we are not directly concerned with them in this discussion.

ments in which specimens of ilmenite and magnetite were held at constant high temperatures for some hours and the products examined with the microscope. What additional information do they furnish about the origin of the set of smaller hematite bodies in the ilmenite? Only a few of these experiments could be considered to have a bearing on this question. They are summarized by Ramdohr as follows: "Die Entmischung I Generation beginnt bei $\backsim$ 700°, die II Generation bei $\ll$ 500° $\lessdot$ 600° rucklaufig zu werden."[14] The statement that the solution of the finer set of hematite gashes commences at a lower temperature than solution of the coarser set might be thought at first glance to give some support to the idea of an inversion, even for a temperature at which it takes place. A consideration of the experiments will show that there is no real justification for this.

If, as appears probable, the hematite bodies are formed during cooling of a solid solution by unmixing followed by aggregation of the unmixed material by diffusion, there seems no reason to suppose that the composition of the solid solutions, along the surfaces between the hematite and ilmenite, would be different in the case of the set of larger bodies than in the case of the set of smaller bodies. Certainly Ramdohr has advanced no reason for supposing so in either of these papers. If there were such a difference it could be due only to a failure to reach equilibrium during cooling whether there was or was not an inversion of the type described above. If the compositions of the pairs of solid solutions in contact along the boundaries are the same they will of course begin to dissolve at the same temperature on heating.

The homogenization experiments cited in the paper (Ramdohr, 1926) give no good reason to believe that solution commences at different temperatures. Ilmenite, showing both sets of hematite lamellæ, after being heated in air for 24 hours at 500°, showed no change that could be recognized even with the highest attainable magnification. After ilmenite had been heated in air 24 hours at 600° it was apparent that solution of the smallest of the hematite gashes had definitely begun. In one specimen of il-

[14] *Op. cit.*, 1926, p. 375.

menite, which had been heated in air for 24 hours at 700°, the set of smaller hematite gashes had almost entirely disappeared. In another specimen from a different locality, after the same treatment the smallest members of this set had disappeared but the larger ones remained. The minutest gashes are by far the most favorable for detecting the solution of a small amount of material. For this reason we should expect solution to be detected there at a lower temperature than on the larger bodies, and it seems to me most probable that this is the explanation of the observations rather than that solution of the large bodies did not begin until about 700°. There is indeed no mention of solution of these bodies in the experiments below 800°. In any case the establishment of an abrupt change in *solubility* would be necessary to the proof of the assumption (an inversion in ilmenite with decreased solubility of Fe_2O_3 below the inversion), whereas what has been established by the experiments (if the oxygen content has remained constant) is an increasing *rate of solution* with rising temperature. Whatever opinion one may hold as to the probability of the origin of the set of smaller hematite bodies in the way assumed, it must be recognized that these experiments give no indication for or against the assumption, much less do they indicate a temperature at which it took place.

In passing it may be noted regarding the temperatures at which the hematite of the gashes formed that in all probability it collected during cooling at a lower temperature than that at which it was found to go back into solution in the experiments (neglecting pressure differences and assuming the oxygen content unchanged). How much lower, the experiments give no basis for opinion.

Where, then, does the temperature 675° come from? This is explained in a footnote to Ramdohr's 1926 paper (p. 375). When the paper was in proof the author learned of the work of Forestier and Chaudron on Fe_2O_3 in which they found a sharp lowering, with addition of Cr_2O_3 or Al_2O_3, of the temperature of the transformation which in pure Fe_2O_3 takes place at about

675°.[15, 16] Ramdohr comments on this as follows: "This transformation appears—compare with the result of my experiments—to be identical with the transformation which gives rise to the unmixing of the second generation."[17] What has been said above, pp. 28–9 (see also, pp. 36–7, appendix), about the bearing of an inversion in ilmenite on an abrupt decrease in the solubility of $FeTiO_3$ in Fe_2O_3 applies equally to this case, the rôles of the $FeTiO_3$ and Fe_2O_3 in the argument being now reversed. It is evident that, whatever this transformation may have to do with unmixing of the hematite solid solutions, *i.e.*, the solutions of ilmenite in hematite, it is not an inversion of ilmenite nor of ilmenite with hematite in solid solution. Consequently it has no bearing on that part of Ramdohr's assumption which is necessary to the argument of Knopf and Anderson, *i.e.*, that there is an inversion[17a] in ilmenite and that the solubility of Fe_2O_3 in the low temperature form of ilmenite is less than in the high temperature form. The argument, as stated by Knopf and Anderson, for a lower limit to the temperature of formation of the ilmenite at Engels is then invalid.

SUMMARY.

The argument of Knopf and Anderson for a lower limit to the temperature of formation of the ilmenite at Engels is based on an assumption by Ramdohr that the set of smaller gashes of hematite, the "second generation," frequently found in ilmenites owes

[15] Forestier, H. et Chaudron, G., Compt. Rend., 180, 1264–66, 1925. The nature of this transformation is open to some question. These authors do not regard it as a phase change.

[16] Sosman, R. B. and Hostetter, J. C., J. Am. Chem. Soc., 38, 831, 1916, report a sharp reversible inversion at 678°. Forestier and Chaudron, *op. cit.*, place the temperature at 675° in good agreement.

[17] "Diese Umwandlung scheint—vgl. auch das Ergebnis meiner Versuche—mit der die Entmischung II Generation veranlassenden Umwandlung identisch zu sein." Ramdohr, P.: *op. cit.*, p. 375, 1926.

[17a] I am indebted to Professor Knopf for drawing my attention to the possible confusion due to the use of the two terms "inversion" and "transformation." The application of the word "inversion" is confined to phenomena of the type described in the third paragraph of p. 28, and again in the appendix. This is the usage at this laboratory and is that recommended by Ferguson (Science, vol. 50, pp. 544–6, 1919). The word "transformation" is of more general application.

its origin to the cooling of a solid solution through an inversion with a sharp decrease in the solubility at the temperature of the inversion. The evidence for this was obtained from microscopic studies of naturally occurring ilmenites. The experiments described in Ramdohr's 1926 paper give no indication for or against this assumption, much less do they fix a temperature at which the inversion occurs.

The temperature 675° cited by Knopf and Anderson as the lower limit to the temperature of crystallization of the ilmenite at Engels is the temperature of a transformation in pure hematite, so the argument by which they seek to fix this lower limit is invalid. We find nothing in their paper or in those cited which fixes a temperature above which the ilmenite containing the scarcely visible hematite lamellæ must have crystallized.

APPENDIX.

DESCRIPTION OF AN EQUILIBRIUM DIAGRAM FOR A HYPOTHETICAL BINARY SYSTEM WITH COMPLETE SOLID SOLUTION AT HIGHER TEMPERATURES, INCOMPLETE MISCIBILITY AT LOWER TEMPERATURES, AND INVERSIONS IN THE END MEMBERS.

The consideration of some features of a hypothetical binary system similar to that suggested by Ramdohr [18] for the system, Fe_2O_3–$FeTiO_3$, may be of service in connection with the preceding discussion. Fig. 2 shows such an equilibrium diagram presenting graphically the temperature-composition relationships at a constant pressure, high enough to prevent the formation of vapor, for a binary system in which the two end members A and B form a continuous series of solid solutions at high temperatures, but at lower temperatures become incompletely miscible in the crystalline state. At still lower temperatures there are inversions in each of the end members, at T_1 in A, at T_2 in B. In each case the temperature at which the inversion takes place is lowered with addition of the second component in solid solution.[19]

[18] Ramdohr, Paul: Beobachtungen an Opaken Erzen. Archiv für Lagerstättenforschung von der Preuss. Geol. Landesanstalt, 34, p. 24, 1924.

[19] For a discussion of the possibilities in binary systems with solid solutions and inversions see Bakhuis Roozeboom, H. W.: Zeit. phys. Chem., 30, pp. 413–429, 1899.

The diagram is divided into fields in each of which the assemblage of phases which is stable throughout the temperature

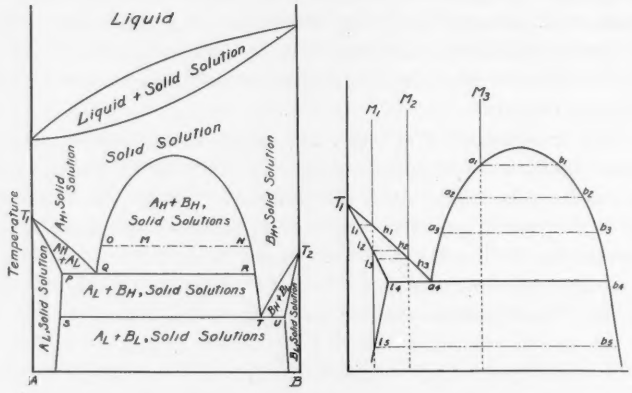

FIG. 2 (left). An equilibrium diagram for a hypothetical binary system. Complete solid solution occurs at high temperatures with unmixing at lower temperatures. Inversions are shown in each of the end members, and in each case the temperature of the inversion is lowered with increasing amounts of the other component in solid solution. The field boundaries are shown by solid lines. A_H and B_H are used to indicate the high temperature forms of the A and B solid solutions; similarly A_L and B_L indicate the low temperature forms.

FIG. 3 (right). A portion of the equilibrium diagram of Fig. 2, on a slightly enlarged scale, drawn to facilitate a description of the behavior of mixtures during cooling.

and composition range represented by the field is indicated by lettering. Each point on the diagram represents both the temperature and composition of a mixture of A and B. The condition of such a mixture at equilibrium is shown by the lettering of the field in which the point lies. When the point lies in a field representing the stability range of two phases, the proportion of the two phases present is equal to the proportion of the segments into which the point divides a horizontal line drawn through the point and extending to the boundaries of the field.

The compositions of the two phases are given by the intersections of this horizontal line with the field boundaries. Thus the point M (Fig. 2) represents a mixture of A and B in the proportion and at the temperature indicated. As shown by the lettering of the field in which it lies, such a mixture at this temperature consists at equilibrium of two solid solutions. The ratio of the amounts of these solid solutions is given by the ratio $MO:MN$ and the compositions of the solid solutions are given by the points N and O. Points on the lines PR and SU represent mixtures which may consist at equilibrium of three phases. The compositions of these are given by the points $P\ Q\ R$ and $S\ T\ U$, respectively, but the ratio in which they exist in any given mixture varies at constant temperature depending on the heat content of the mixture. We shall return to this later.

Let us now make use of the diagram to trace the behavior of some typical solid solutions during cooling. As an aid to this a portion of the diagram has been reproduced on an enlarged scale in Fig. 3. Consider a solid solution the temperature and composition of which are represented by the point M_3. As the material is cooled the point representing the temperature and composition moves along the perpendicular through M_3. Until the temperature of the material falls below that indicated by the intersection of this perpendicular with the field boundary, the material consists of a single phase. However, when this point crosses the field boundary and enters the field labelled $A_H + B_H$, a second solid solution appears. The compositions of these solid solutions, when the temperature is infinitesimally below that indicated by the field boundary, are given by the points a_1 and b_1. As cooling progresses, more and more of the second phase is formed, the compositions of both phases continually changing (at equilibrium) and becoming successively a_1 and b_1, a_2 and b_2, etc. Below the temperature represented by the line a_4b_4 the high temperature form of the A solid solution is no longer stable, so at this temperature, with continued loss of heat, the low temperature form of the solid solution, represented by the point l_4, separates from the high temperature form, represented by the point a_4, with accompanying liberation of more B solid solution, of the composition indicated

by b_4. When all the high temperature form of the A solid solution has been converted to the low temperature form plus B solid solution, further loss of heat is accompanied by decrease of temperature and by corresponding further change of composition of the two solid solutions along the curves l_4l_5, b_4b_5.

If a solid solution represented by the point M_2 be cooled it will remain a single phase until the temperature falls just below that indicated by the curve T_1a_4, when the low temperature form of the solid solution begins to separate. With further loss of heat the material continues to invert to the low temperature form, the temperature falling and the compositions of the two solid solutions following along the curves l_3l_4 and h_3a_4. At the temperature represented by the straight line $l_4a_4b_4$ there still remains some of the high temperature form. With further loss of heat a third phase, B solid solution represented by b_4, appears and as heat is removed continues to separate, together with the low temperature form of the A solid solution represented by l_4, the temperature remaining constant. When all of the high temperature form of the A solid solution represented by a_4 has been converted to the solid solutions represented by l_4 and b_4, further loss of heat will lower the temperature. This lowering of temperature will be accompanied by progressive unmixing of the two solid solutions, their compositions following the same course as those derived from the solid solution represented by M_3.

If a solid solution represented by the point M_1 be cooled, just as in the case of M_2 inversion begins when the temperature falls infinitesimally below that indicated by the curve T_1a_4, but in this case all the material will have changed to the low temperature form when the temperature l_2 is reached. No B solid solution will be formed until the temperature reaches that indicated by the point l_5 on the field boundary l_4l_7.

In the cooling of the solid solution represented by the point M_3 we found two solid solutions separating out above the inversion temperature. The inversion of the A solid solution took place at a single temperature and added to the amount of B solid solution by liberating more. Any bodies into which the B solid solution had collected would, however, remain unchanged in com-

position through this inversion. Below the temperature of this inversion there is of course progressive unmixing of both solid solutions in the same way as above it. Any solid solution, the composition of which lies between that indicated by a_4 and that indicated by b_4, will behave similarly during cooling.

In the cooling of the solid solution represented by the point M_2 the inversion of the high temperature form of A solid solution to the low temperature form took place in part over a range of temperatures, in part at a constant temperature. At this constant temperature B solid solution formed for the first time, being liberated by the inversion of the high temperature form of the A solid solution to the low temperature form. Any solid solution, the composition of which lies between that indicated by l_4 and that indicated by a_4, will behave similarly during cooling.

In the cooling of the solid solution M_1 the inversion from the high to the low temperature form took place over a range of temperature, but there was no separation of B solid solution until a lower temperature was reached. Any solid solution, the composition of which lies between that of pure A and that indicated by the point l_4, will behave similarly during cooling.

It would be a needless repetition to trace the cooling of these materials through the temperature range of the inversion in the B solid solutions since the behavior of the materials, as they are cooled through this temperature range, is similar to their behavior during cooling through the temperature range of the inversion in the A solid solutions, the rôles of the two solid solutions being reversed.

Nothing has so far been said about the size of particles into which the phases collect under a given heat treatment. The equilibrium diagram represents only the temperature and composition relationships of the phases, so does not indicate this. Consider, for example, the product formed by cooling the solid solution represented by M_3 to the temperature indicated by a_2b_2 and suppose the equilibrium has been closely approached. The two phases may be in submicroscopic units so that the product appears microscopically homogeneous, or by diffusion one of them may have collected into bodies of considerable size such as those

composing the coarser set of hematite gashes frequently to be seen in ilmenite. Let us suppose the latter condition to obtain. With continued cooling each of the phases unmixes further with separation of the other solid solution, *B* solid solution separating in the bodies of *A* solid solution and vice versa. Whether this newly separated material will remain submicroscopic, collect and become visible as smaller bodies within the larger, or diffuse to build up the large earlier-formed bodies, the diagram does not indicate. Nor does it indicate what will be the state of aggregation of the two phases which form at constant temperature from the solid solution represented by the point a_4. The experience gained during the experimentation necessary to determine equilibrium in a given system will in many cases permit a reliable estimate of the state of aggregation under a given treatment, but this cannot be read off the equilibrium diagram.

In any actual case cooling will probably be too rapid for *complete* equilibrium to be maintained. *Complete* equilibrium is indeed seldom if ever reached, for the rate of approach to equilibrium drops off as the condition is approached. However, the departure from it may be negligible and always is in a definite direction. (In experimental work the condition at equilibrium is established within limits which in many cases may be made very narrow by approaching it from opposite directions.) Therefore a knowledge of the equilibrium relationships in a system, while not permitting us to predict fully the condition of a given material under a given heat treatment, does show the direction in which the reactions will proceed. It is largely for this reason that our knowledge of equilibrium, confined though it is to relatively simple systems, has been of great value in unravelling the history of the complex assemblages of phases that make up rocks or mineral deposits.

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A MICROSCOPIC STUDY OF ORES FROM THE CAMPBELL MINE, BISBEE, ARIZONA.[1]

G. M. SCHWARTZ AND C. F. PARK, JR.

INTRODUCTION.

THE data on which the main portion of this paper is based were obtained from an excellent suite of specimens furnished by Mr. William P. Crawford, Assistant Engineer, of Bisbee. The specimens represent most of the important phases of the Campbell ore body of the Calumet and Arizona Mining Company. The description of the structural features of the mine is taken entirely from data supplied by Mr. Crawford. The Campbell ore body is a recent discovery and therefore practically nothing has been published regarding it. We are deeply indebted to Mr. Crawford as well as to Mr. H. A. Clarke, Manager, and Mr. H. M. Lavender, Chief Engineer, Calumet and Arizona Mining Company, for the opportunity to place on record some of the features of the ores from this remarkable deposit. It has been referred to by Joralemon [2] as one of the major discoveries of recent years, and is classed by him with the discoveries at Cananea, the deep ore bodies at the Frood Mine, Sudbury, Noranda, Roan Antelope, N'Kana, N'Changa and Mufulira.

THE CAMPBELL ORE BODY.

The Campbell mine, according to Mr. Crawford,[3] is about 2300 feet southeast of the Junction shaft of the Calumet and Arizona group. The ore body as developed at present is mainly in the Escabrosa limestone, but some ore has been found in the Naco

[1] Presented by Title, Society of Economic Geologists, Toronto Meeting, December, 1930.

[2] Joralemon, Ira B.: The Unexpected in the Discovery of Ore Bodies. Amer. Inst. Min. Eng., Tech. Paper 340, 1930.

[3] Personal communication.

limestone above and in the Martin limestone beneath the Escabrosa.

The main ore lens has been partially developed from the 1500 level down to the 2200 level, a vertical distance of 700 feet. Probable extensions of the main lens have also been found on the 1300, 1400 and 2300 levels. The main lens as developed on the 1600, 1700, and 1800 levels has an average length of about 500 feet and a width varying from 50 to 250 feet. Besides the main lens there are several minor ore bodies having a smaller area and vertical extent.

On the upper levels the ore bodies are separated by limestone, but on the lower levels the limestone has been largely replaced by pyrite, and the ore bodies are arranged around the periphery of a mass of pyrite. The axis of the main lens strikes northwest and the dip is northeast. Below the 1700 level the dip of the footwall is nearly 90°, but above the footwall roughly conforms to the dip of the limestone, or about 25°. The hanging wall is irregular, but at places follows the limestone bedding.

The footwall is not sharply defined but is a gradational zone varying in width from one foot to fifteen feet. The zone passes outwardly from the sulphide copper ore through bunches of copper ore mixed with lead-zinc sulphides into hematite and recrystallized limestone and finally into unaltered limestone. Hematite is present wherever the footwall has been cut, but its character varies from a hard compact variety to a soft micaceous hematite resembling graphite. The hematite may be present as a solid seam or as disseminations in recrystallized limestone.

The hanging wall is irregular and the ore at places grades into silica and pyrite. At other places there is a well-defined wall, usually silicified.

At the north end of the ore body an oxidized zone extends from about 50 feet above the 1600 level to the 2000 level. Present development shows the greatest extent of this oxidized zone to be between the 1600 and 1800 levels. In this area cuprite, malachite, and native copper are intimately associated with the sulphides. There is also scattered oxidation along fractures in the main ore body.

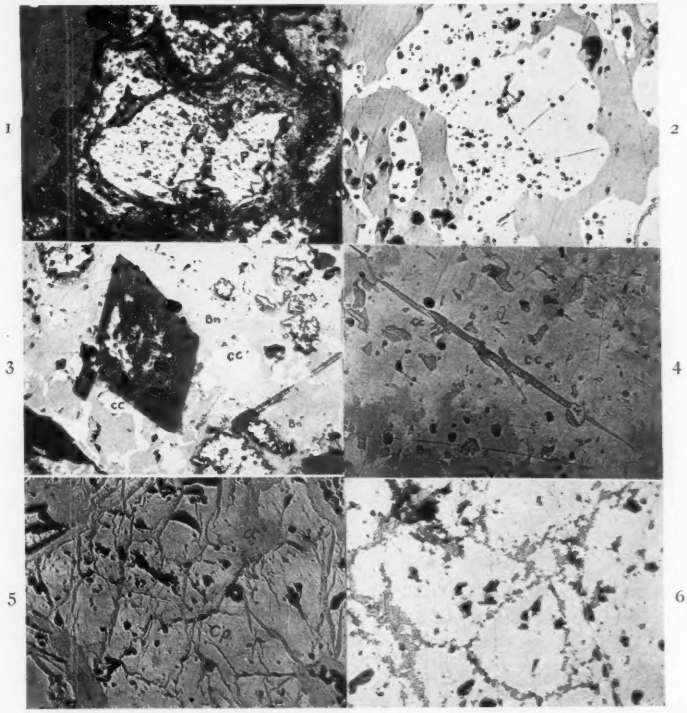

FIG. 1. Pyrite (*P*) surrounded by concentric bands of hematite (*H*). A small zone of chalcopyrite occurs between pyrite and hematite. The hematite is evidently a result of replacement of chalcopyrite in this case but also replaces pyrite elsewhere in the specimen. 1900 level. × 72.

FIG. 2. Chalcopyrite (white) replaced by bornite. The relation is typical of the mixed iridescent bornite chalcopyrite ore. 2000 level. × 36.

FIG. 3. Euhedral carbonate crystal in sulphide. Crystal encloses sulphide also. Sulphides are pyrite (*P*), bornite (*Bn*), and chalcocite (*Cc*). 2200 level. × 72.

FIG. 4. Typical blade of stromeyerite (*Sr*) in chalcocite (*Cc*) which has replaced bornite (*Bn*). The blade of stromeyerite is cut by a small grain of tetrahedrite (*T*). 1700 level. × 44.

FIG. 5. Chalcocite (*Cc*) directly replacing chalcopyrite (*Cp*). This is believed to be supergene replacement. 1900 level. × 36.

FIG. 6. Sphalerite (dark gray) more or less surrounding grains of chalcopyrite. Suggestive of replacement, but possibility of unmixing must be considered. 2200 level. × 36.

The south end of the main ore body is limited by the Mexican Canyon fault. The magnitude of throw of this fault has been variously calculated from 50 to 500 feet. The absence of good markers makes it difficult to calculate a definite throw but it is probably between 50 and 150 feet with the principal movement pre-ore. Some post-ore movement is recognized.

Pre-ore movement along this fault should not be regarded as definite evidence in favor of post-Cretaceous mineralization and is offered as field evidence only. The fault as cut on different levels of the Campbell shows little variation in dip and strike. Recent development work in adjacent Denn ground has shown a fault having a similar dip and strike, which is evidently an extension of the one in the Campbell area. The intersection of this with the Dividend fault has been found and future development work north of the Dividend fault will render possible better correlation of the fault systems.

It is probable that there was movement along the Mexican Canyon fault line at about the same time as the Dividend faulting. Later there was another period of movement along the same zone, which faulted the Cretaceous beds, but with a lesser movement south of the Dividend fault.

On the 1700 and 1800 levels is an area of oxidized ore south of the fault. Native copper is an important ore mineral in this area. On the 1800 level chalcocite is abundant, with native silver along fractures.

THE ORES.

The ores utilized in this study came from nearly all parts of the main and subsidiary ore bodies and wall rocks. Much of the ore shows a noteworthy lack of gangue minerals. The most abundant phase of the ore, according to Mr. Crawford,[4] is a massive chalcopyrite which appears rather pure, but as is usually the case, proves not so pure when observed on a polished surface. Pyrite and quartz are the common valueless minerals. Next to the chalcopyrite in abundance is a massive bornite-chalcocite ore which, though commonly appearing to be mainly bornite, contains

[4] Personal communication.

much chalcocite with lesser amounts of other minerals. There are some large stopes of this material of unusual richness. A common phase is a mixed bornite-chalcopyrite ore of a peculiar iridescence (Fig. 2) due to the fine-grained mixture of the two minerals. Its peculiar appearance even led to the suggestion that it might be a mineral intermediate between bornite and chalcopyrite. Near the edges of the ore bodies, massive to granular pyrite is common. The actual contact or border phase is predominantly specular hematite at some places with an intimate mixture of copper, lead, and zinc sulphides. A siliceous material forms a border phase at places and also occurs within the ore bodies. Oxidation is not uncommon along faults and the borders of the ore body as well as in some of the smaller detached bodies. Consequently there are many variations in the ore due to oxidation and secondary sulphide enrichment.

Sooty chalcocite is commonly present along fractures. It seems clearly to have replaced chalcopyrite without intermediate minerals (Fig. 5). The relations of chalcocite to bornite and other minerals are determinable only on polished surface and are described below. One unusual specimen shows native silver coating a fracture surface of chalcocite. Native silver and cerargyrite were also observed in a reddish siliceous rock that seems to represent the oxidation of a siliceous-pyritic phase. This is an intermediate phase between the border zone and the main body of the ore. The hematite of the border phase is commonly coated with limonite. Soft earthy limonite and hematite are found along fractures. At places malachite, azurite, cuprite, native copper and manganese oxide occur along fractures.

The ores seem to be somewhat unusual in containing small amounts of tellurium, but no tellurium minerals were observed. The silver content is notably high at places and the minerals responsible for this are described below.

ORE MINERALS.

The principal sulphide minerals found in the Campbell ore, approximately in the order of abundance, are: chalcopyrite,

bornite, pyrite, chalcocite, sphalerite, galena, stromeyerite, tetrahedrite, enargite, famatinite and covellite. Niccolite (?), native copper, native silver, cuprite, malachite, azurite, cerussite and cerargyrite were also observed. Hematite, especially specularite, is abundant in the border phases. Both hematite and limonite occur in the oxidized ores.

The ores furnish excellent examples of many of the characteristic relationships found in copper ores, as well as a few more unusual features.

Pyrite occurs as nearly pure crystalline masses and as more or less broken and corroded or rounded grains, surrounded and evidently replaced by chalcopyrite, galena, sphalerite, and chalcocite. In many specimens quartz surrounds the pyrite grains with little evidence of replacement. The pyrite granules may be badly shattered and the fractures filled by chalcopyrite or more rarely by other sulphides. A good example was observed of sphalerite cementing the pyrite fragments. This shattering may, at least partially, be due to replacement, as suggested by Wandke.[5] Distinct shattering or brecciation with subsequent re-cementation, both of the sulphide ore and of the pyritic mass, has been observed on the 2200 level and is probably present elsewhere. In many specimens the fractures form remarkably regular systems.

Mr. Crawford notes that in some parts of the ore body a regular system of fracturing is discernible. The fractures are parallel in dip and strike to the Mexican Canyon fault, and may have been present in the limestones before replacement by the sulphide copper minerals. Polishing indicates that in places there has been some post-ore movement. Where the fractures are more pronounced, the ore breaks into regular blocks and in nearly every observed instance the blocks show a darkening or tarnish along the fracture planes. This may have resulted from alteration, or may indicate a slight post-ore movement which ground the ore a sufficient amount to tarnish it but not enough to cause polishing of hand specimens.

In a few specimens some euhedral grains of pyrite were noted. These are probably of a later age and thus escaped brecciation.

[5] Wandke, A.: Shattering by replacement. ECON. GEOL., vol. 20, pp. 60–87, 1925.

Pyrite with more or less quartz is commonly found at the borders of the main ore body. Some specimens show no sulphide other than pyrite. The relationships described above indicate that pyrite was the first sulphide to form.

Chalcopyrite is quantitatively the most important ore mineral. Many specimens show nearly pure massive chalcopyrite but as a rule disseminated crystals and rounded grains of pyrite occur in this massive material. Small amounts of gangue are also commonly present, and in some cases quartz forms a matrix for irregular areas of chalcopyrite. Bornite is the usual associate of chalcopyrite, and the two often occur with smooth and curving boundaries, suggestive of a mutual relation. At these places there are about as many residual spots of chalcopyrite in bornite as of bornite in chalcopyrite. As a rule, however, the bornite appears to have replaced the chalcopyrite (Fig. 2). In many specimens chalcopyrite changes directly to chalcocite, with no intermediate minerals. This alteration was observed in specimens that were more or less porous, and the chalcocite developed along a network of veinlets (Fig. 5). Part of the chalcocite is somewhat sooty, suggesting that the replacement was due to supergene processes. This direct replacement of chalcopyrite is not the rule in copper ores, bornite usually intervening, but an example has recently been described by Davidson.[6] Under high magnifications irregular inclusions of bornite were observed in this chalcocite, but scarcely enough to indicate that the replacement took place with bornite as an intermediate product.

Chalcopyrite at places also fills fractures in the early quartz gangue. Chalcopyrite from the Campbell ore body as a whole appears to be hypogene (with the exception of a small amount in cross-cutting fractures in bornite).

Hematite (specularite) is found chiefly near the borders, especially the footwall, of the main ore body. Minor amounts are found in the hanging wall of the main ore body and in the border phases of the smaller lenses. These occurrences are sporadic and are not as well defined as in the footwall. It occurs as radiating

[6] Davidson, D. M.: The Geology and Ore Deposits of Chambishi, Northern Rhodesia. ECON. GEOL., vol. 26, pp. 131–152, 1931.

needles or plates which form rudely concentric structures. The mineral appears to have been formed in some cases by hydrothermal alteration of pyrite. In a few specimens it seems that chalcopyrite has partially replaced pyrite, and the chalcopyrite has in turn been almost completely replaced by hematite (Fig. 1). Specular hematite is one of the most important minerals in the border zones of the ore body. This is suggestive of moderately high temperature of formation, but is not unusual in Arizona copper ores. Specularite later than chalcopyrite has been described from the Iron Cap mine in the Globe district.[7]

Earthy hematite is also found in some of the oxidized areas and is clearly of supergene origin. Large masses of ores appear in hand specimen to be mainly bornite, but as a rule other minerals are found to be abundant.

Bornite, as indicated above, may be partly contemporaneous with chalcopyrite but as a rule appears to be later, and replaces chalcopyrite. The tendency of chalcopyrite and bornite to develop mutual boundaries and of bornite to invade chalcopyrite indicates hypogene replacement. Bornite probably also forms on a small scale as a supergene mineral, replacing chalcopyrite. Bornite is commonly accompanied by chalcocite, a fact which is often not evident before polishing. The chalcocite clearly replaces the bornite, mostly forming a network of irregular veinlets.

Several of the bornite specimens examined came from a stope of high grade ore on the 1700 foot level. This material deserves special description, as it runs very high in copper and contains considerable silver, which is found to be present mainly as stromeyerite. Some of the bornite contains considerable chalcocite which is later than the bornite and fills irregular cross-cutting veinlets (Fig. 3). More rarely the bornite is present as small rounded "residual" grains, surrounded entirely by chalcocite. Under the oil immersion lens a coarse subgraphic intergrowth of chalcocite and bornite may be seen.

Small amounts of sphalerite are present as rounded grains within the bornite. Much of it occurs in fractures that cut

[7] Schwartz, G. M.: Microscopic Replacement versus Injection of Ores. Amer. Min., vol. 12, pp. 297–304, 1927.

chalcopyrite and is therefore later than the chalcopyrite. The formation of these minerals may have taken place through a considerable length of time, and an overlap in their deposition has occurred.

Pyrite is present as rounded or shattered grains surrounded by bornite or chalcocite. An occasional small rounded spot of a reddish mineral, probably niccolite, may be seen within the bornite.

The chalcocite areas that cut the bornite are in turn cut by blades of stromeyerite. Rounded spots of tetrahedrite, tennantite, enargite, and smaller quantities of famatinite are also present in the chalcocite. These minerals are in very small quantities although widely distributed. Most of them are confined to the chalcocite areas, but occasional spots may be observed in the bornite. It is difficult to interpret their relationships.

The antimony-arsenic minerals mostly occur as rounded grains, but in a few places well defined blades are developed. These blades occur almost entirely within the chalcocite and usually stop abruptly against bornite. Stromeyerite is also present as blades in chalcocite. The silver mineral may stop abruptly against the antimony-arsenic minerals, then continue after an interval (Fig. 4). This may be interpreted to mean that the stromeyerite is earlier than the arsenic-antimony minerals. There is no other evidence in favor of this theory. At a few places coarse, subgraphic intergrowths of these minerals occur. Stromeyerite may also form a somewhat finer, subgraphic intergrowth with chalcocite. Tetrahedrite, tennantite, enargite, and famatinite may also form coarse subgraphic intergrowths with chalcocite.

There is also a triangular intergrowth of bornite and chalcocite that suggests replacement, although without further data the order of replacement can not be definitely stated. One other possibility that has to be considered is that the triangular texture may have resulted from the unmixing of a solid solution.[8]

Stromeyerite, in the Campbell ore, was found in specimens of bornite with smaller areas of chalcocite. It was also observed in specimens from the Junction mine that are high in chalcocite

[8] Schwartz, G. M.: Experiments Bearing on Bornite-chalcocite Intergrowths. ECON. GEOL., vol. 23, pp. 381–397, 1928.

It is the only silver mineral identified except native silver and cerargyrite in some of the oxidized ores.

The identification of stromeyerite gave considerable difficulty. It was first identified as pearceite by the use of determinative tables and the fact that stromeyerite was previously reported as not etched by light. Later work on the etching tests of silver minerals by M. M. Stephens[9] indicated that the mineral was stromeyerite. Dr. M. N. Short kindly loaned us his standard specimens of pearceite and stromeyerite for comparison. The effect of the full strength of an arc light (with no heat filter present) on a polished surface proves conclusively that the mineral is not pearceite but stromeyerite.

As described above, stromeyerite occurs as blades cutting chalcocite and also as irregular areas (Fig. 4). It seems to be in part later than chalcocite and the other sulphides. Irregular inclusions in chalcocite may well be contemporaneous with it. Stromeyerite occurs so closely related to the antimony-arsenic minerals that it seems probable that its origin is the same, that is hypogene.

Stromeyerite is apparently not very abundant in ore deposits in general. Guild[10] has summarized its occurrence in polished ores and finds that the common modes of occurrence are (1) associated with tetrahedrite (freibergite) and doubtless derived from it, and (2) as a replacement product of bornite. Neither occurrence seems to be necessarily limited to either a hypogene or a supergene origin so that the mineral itself is not indicative of a definite origin. So far as its occurrence in the Campbell ore is concerned it seems clearly of the same origin as the chalcocite in which it is found, and the antimony-arsenic minerals with which it is associated.

From the field occurrence as well as the microscopic associations and relationships cited above, it is thought that practically all the minerals found in the bornite ores are hypogene. These

[9] Stephens, Maynard M.: Effect of Light on Polished Surfaces of Silver Minerals. Amer. Min., vol. 16, pp. 532–549, 1931.

[10] Guild, F. N.: A Microscopic Study of Silver Ores. ECON. GEOL., vol. 12, pp. 298–340, 1917. The Enrichment of Silver Ores. Laboratory Investigation of Ores, pp. 200–239. McGraw-Hill, 1928.

include bornite, chalcocite, tetrahedrite-tennantite, enargite, famatinite, niccolite and stromeyerite.

Sphalerite and galena are found chiefly in the border phases of the ore body. They are of minor importance commercially. In a few places stringers of galena may be seen cross-cutting sphalerite. More commonly, however, the boundaries are mutual, and small spots of one mineral may be surrounded by the other. The two minerals seem to be practically contemporaneous with galena, continuing to form after the zinc sulphide was deposited.

In several specimens sphalerite may be observed forming a thin border or outline around chalcopyrite grains (Fig. 6). It appears to replace the chalcopyrite. In at least one place this condition is reversed, and the copper mineral forms a narrow band around the zinc sulphide granules. Such a texture is known to develop from an unmixing of two minerals, as shown by some recent experiments of the senior author.[11] This is, therefore, one of the origins that it is necessary to consider.

One area of graphic intergrowth between galena and chalcopyrite was noted. The relative ages were not clear, but in other sections chalcocite appears to replace galena, forming small grains in the galena, but always associated with holes or fractures. This conclusion may be extended to the chalcocite of the intergrowth as there is no evidence of contemporaneous deposition of galena and chalcocite.

Chalcocite, due to its occurrence and association with other minerals of the ores, especially the arsenic-antimony sulphides, is thought to be largely of hypogene origin. Some of the sooty material from the oxidized areas is undoubtedly supergene.

The chalcocite all seems to show orthorhombic etch cleavage, but there is great variation in the size of grain. That classed as hypogene is relatively coarse-grained, whereas that believed to be supergene is very fine-grained.

One specimen of chalcocite from the 1800 level south of the Mexican Canyon fault shows much native silver along fractures. Much of the native silver is coated with cerussite, occurring as

[11] Schwartz, G. M.: Intergrowths of bornite and chalcopyrite. ECON. GEOL., vol. 26, pp. 186–201, 1931.

thin films and small twinned crystals. Oxidation has been active in the area and probably accounts for the native silver which was precipitated by the chalcocite. This chalcocite shows a series of concentric or pisolitic structures believed to have been formed during the replacement of original minerals. These structures are believed to be characteristic of some supergene chalcocite. They have been observed by the authors in chalcocite from the Old Dominion mine, Globe, Arizona.

Considerable oxidation has occurred even in the deepest part of the ore body as shown by the presence of native copper and limonite on the 2200 level. The minerals definitely determined as supergene, in addition to the sooty chalcocite and possibly some bornite, are covellite, copper carbonates, cerussite, "limonite," manganese oxides, native copper and cuprite. Native silver and cerargyrite are present in small quantities.

In the sulphides, covellite occurs as small spots clearly associated with fractures and in more or less oxidized ores. It is believed to be supergene in all the observed occurrences.

Native silver was also found in small amounts in the siliceous hematite-stained material from the 1900 level. Small amounts of cerargyrite were observed in the hand specimen of this material, but the silver can be seen only on the polished surface.

Native copper and cuprite are associated with the limonitic and earthy hematite ores. Occasional stains of malachite are also present. A common product of oxidation is soft yellow "limonite" with all original structure gone and now loose and earthy. Some earthy hematite also occurs, but is not as common as "limonite" in the specimens available, which came mainly from a stope on the 2200 level.

The gangue minerals present in the sulphide ores are largely quartz and the carbonates, calcite and mangano-siderite. Quartz is early, even earlier than the first pyrite. Later silicification has taken place after the formation of most of the ores. Euhedral crystals of carbonates may be present in the sulphides (Fig. 3). These crystals may be replaced, usually internally, by sulphides, and grade from complete crystals to mere skeleton outlines.

CONCLUSIONS.

Considered as a whole, the ore body of the Campbell area is composed mainly of chalcopyrite with important masses of bornite and chalcocite. Near the borders of the ore, sphalerite and galena become increasingly abundant. As these in turn decrease, specular hematite becomes prominent to the almost complete exclusion of the sulphides. Only very small amounts of pyrite are seen in association with the specularite, and from the appearances in polished sections it is thought that the pyrite has changed to hematite (Fig. 1).

The general order of paragenesis of the hypogene sulphide minerals is pyrite, chalcopyrite, bornite, chalcocite with tetrahedrite, tennantite, enargite, famatinite and stromeyerite closely connected with chalcocite in origin. Stromeyerite also seems in part later than chalcocite. Bornite may be in part contemporaneous with chalcopyrite. The two are very closely related, whatever the exact interpretation. In the border phases, where sphalerite and galena appear abundantly at places, they seem to follow chalcopyrite and bornite with galena later than sphalerite. The specularite of the border phase seems to follow pyrite and chalcopyrite where these minerals are in juxtaposition.

The principal supergene sulphide is chalcocite. It replaces chalcopyrite and bornite. Small amounts of supergene bornite form where chalcocite replaces chalcopyrite. Covellite occurs only in very small amounts and appears to be always connected with oxidation.

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COVELLITE–CHALCOCITE SOLID SOLUTION AND EX-SOLUTION.

ALAN M. BATEMAN AND SAMUEL G. LASKY.

INTRODUCTION.

THE investigation of minerals that make up ore deposits and the interpretation of experimental products that resemble natural occurrences, are of wider interest than the mere solution of the origin of individual ore minerals. Such studies help in deciphering the genesis of ore deposits. The following pages, it is hoped, throw light on the origin of copper deposits that contain covellite and chalcocite.

This paper presents the continuation of an interrupted study started several years ago. Some results were given in a preliminary paper.[1] Subsequently the work was continued, and a part of it was assigned to Mr. Lasky as a problem for part of an essay for the Master of Science degree at Yale University. All the later experimental work and considerable of the discussion of the results were contributed by Mr. Lasky. Professor Paul Kerr of Columbia University was good enough to make X-ray studies of some of the material.

THE PROBLEM AND ITS BEARING.

For years there has been interest among geologists in ore deposits that contain chalcocite. For a long time this mineral was commonly considered diagnostic of secondary or supergene enrichment, and therefore superficial in distribution. However, a primary or hypogene origin has been advocated for the chalcocite of several deposits and it is now generally accepted that this mineral is a primary constituent of some ore deposits.

[1] Bateman, Alan M.: Some Covellite-Chalcocite Relationships. ECON. GEOL., vol. 24, pp. 424–439, 1929. Presented before the Society of Economic Geologists at the New York meeting, December, 1928.

But there still persist differences of opinion as to what constitutes proof of a hypogene origin. The presence of isometric chalcocite in the ores is, in most cases, *prima facie* evidence of a hypogene origin, since it indicates a temperature of formation above 91° C.[2] However, this mineral is rare; the orthorhombic or low-temperature form is the common one. The latter indicates either (*a*) formation by low-temperature supergene processes; (*b*) formation by hot solutions but below a temperature of 91° C.; or (*c*) original formation at temperatures above 91° C. and inversion upon cooling to the orthorhombic form. To distinguish between these is commonly difficult. Therefore, any additional criteria that indicate whether the chalcocite is hypogene or supergene will help to elucidate the conditions of formation of the deposit that contains it. Several such criteria have recently been discussed by Bateman.[3] Another one is a type of natural intergrowth between chalcocite and covellite which is interpreted as having been formed by unmixing from a solid solution of the two substances. In some earlier experiments[4] it was found that in natural intergrowths of covellite and chalcocite, the covellite readily disappeared into the chalcocite upon heating, apparently going into solid solution. Subsequent cooling caused unmixing, giving rise to characteristic microtextures[5] of chalcocite and covellite. These resemble some of those found in mineral deposits. If, then, similar processes have operated to produce the natural occurrences, they will indicate either a hypogene origin for these minerals, or that solid solution of supergene minerals has been induced by subsequent heat metamorphism with later cooling.

However, the earlier experiments fell short in not showing that unmixing of covellite from induced solid solutions could be made to take place at will. Also, the nature of the changes that took

[2] Posnjak, Allen, and Merwin: The Sulphides of Copper. ECON. GEOL., vol. 10, pp. 491–535, 1915.

[3] Bateman, Alan M.: The Ores of the Northern Rhodesian Copper Belt. ECON. GEOL., vol. 25, pp. 365–418, 1930.

[4] Bateman, Alan M.: Some Covellite-Chalcocite Relationships, *op. cit.*

[5] For use of terms microtexture and microstructure, see Bateman, Alan M.; the ores of the Northern Rhodesia Copper Belt. ECON. GEOL., vol. 25, p. 394, 1930.

place was not understood. Consequently, it could not be inferred with certainty that the natural intergrowths may have originated by unmixing from similar solid solutions originally formed at elevated temperatures. It became evident that more experimental work was necessary; and, particularly, the natural products had to be studied further to determine if a solid-solution stage is compatible with their earlier history, and if they exhibit evidence, other than the intergrowths themselves, that these minerals had once been in solid solution.

The following pages, therefore, deal with the continuation of these experiments and with theoretical discussions of the problems raised. It will be shown that ex-solution can be brought about as consistently as solid solution and an explanation is offered of the manner in which such natural solid solutions were formed. This explanation, however, is based upon a critical study of natural products, and for this purpose the ores of Kennecott, Alaska, were singled out. Consequently, it will be necessary first to recall briefly to the reader some features of the occurrence and character of the Kennecott ores.

OCCURRENCE OF KENNECOTT ORES.

The Deposits.—The copper deposits of Kennecott, Alaska,[6] consist of steeply inclined replacement veins and irregular replacement bodies inclosed in dolomitic limestones of Triassic age. These beds overlie a thick series of altered basaltic lava flows, and dip gently. Some quartz-diorite intrusives, later in age than the ore, occur in the general vicinity. The ore bodies strike parallel to the dip of the beds and are confined to the lower few hundred feet of the dolomitic beds; a few project downward into the basal limestone. The veins range in width from a few inches to over 100 feet. They are commonly widest near their bottoms and pinch to mere cracks at a certain distance up their dip from the base of the dolomitic beds, but have been followed down the pitch, parallel to the dip of the beds, for over 4000 feet. Their vertical

[6] Abstract from Bateman, Alan M. and McLaughlin, D. H.: Geology of the Ore Deposits of Kennecott, Alaska. ECON. GEOL., vol. 15, pp. 1–80, 1920.

extension is thus quite limited; few outcrop on the surface and many do not reach within a thousand feet or more of the surface.

The ore consists of copper sulphides and calcite. There are masses of chalcocite from 2 to 80 feet in width and hundreds of feet in length which will run, as mined, from 30 to 78 per cent copper. These may be flanked by lower grade ore.

Massive, hard, brilliant chalcocite is the chief ore mineral; covellite is fairly abundant. Small amounts of enargite, bornite, chalcopyrite, tennantite, luzonite, and an unidentified mineral are present. A few specks of pyrite, sphalerite, and galena have been seen. Silver is contained in the chalcocite. Oxidized products, chiefly malachite and azurite, are scattered throughout most of the deposits. The iron and silica content of the ore is only a fraction of one per cent. Consequently, the original metallization consisted almost entirely of copper, sulphur, and silver, with small quantities of arsenic and iron and rare traces of other metals. The ore is thus quite unusual.[7]

The ore minerals are considered to have been deposited from solutions at a temperature above 91° C. Recent work in this laboratory indicates that an early conception of possible colloidal origin[8] of the copper sulphides now seems highly probable; it is considered that the copper sulphides were transported as colloids[9] in a highly dispersed condition and were flocculated upon reaching the limestone, thus accounting for many of the peculiar microtextures exhibited by the Kennecott ores.

The Minerals.—Of the ore minerals mentioned, chalcocite is predominant. With the exception of covellite, the other minerals are comparatively rare. The general order of precipitation of the minerals is: chalcopyrite, chalcopyrite and bornite, bornite, bornite and sulpharsenides, covellite, covellite and chalcocite, and chalcocite. Subsequent alteration gave rise to oxidation products and a little supergene chalcocite and covellite.

There are many interesting intergrowths in the ores, some of

[7] For more detailed mineralogy, consult Bateman and McLaughlin, *op. cit.*

[8] Bateman and McLaughlin, *op. cit.*, p. 66.

[9] Lasky, S. G.: A Colloidal Origin of Some of the Kennecott Ore Minerals. ECON. GEOL., vol. 25, pp. 737–757, 1930.

which have already been described.[10] It is not the purpose of this paper to discuss all these intergrowths; only those that have a particular bearing on the problem under consideration, namely, the chalcocite-covellite intergrowths, will be briefly mentioned. These, and the chalcocite by itself, offer supporting evidence of natural solid solution and ex-solution.

MICROSCOPIC FEATURES SUGGESTING SOLUTION AND EX-SOLUTION IN THE KENNECOTT ORES.

The Chalcocite.—The Kennecott chalcocite was earlier considered to be hypogene [11] on the basis of detailed field evidence, microscopic examination, and chemical considerations. Isometric partings, evident in some hand specimens and disclosed in others by etching, indicated that some of it is in the isometric form or had an isometric ancestry. Some of it gave no evidence of either isometric or orthorhombic symmetry. Subsequently, the adaptation of polarized light to the reflecting microscope afforded positive identification and confirmation of the earlier conclusions; most of the Kennecott chalcocite has been found to be isotropic and therefore isometric. It remains evenly dark upon rotation of the stage under crossed nicols with reflected light, and is in marked contrast to most other chalcocite, which shows anisotropism with the same procedure. Consequently it is the high-temperature form and is definitely of hypogene origin.

Posnjak, Allen, and Merwin [12] have shown that chalcocite formed above 91° C. is isometric, but if formed below 91° C. it is orthorhombic. Normally the isometric form changes over to the orthorhombic when the temperature drops below the inversion point of 91° C. They showed, however, that 8 per cent. or more of covellite in solid solution with isometric chalcocite prevents its inversion and it remains in the isometric form at normal temperatures. From this it follows that natural isometric chalcocite

[10] Bateman and McLaughlin, *op. cit.*
Bateman, Alan M.: Some Covellite-Chalcocite Relationships, *op. cit.*
Lasky, S. G.: *op. cit.*

[11] Bateman and McLaughlin, *op. cit.*, 1920.

[12] *Op. cit.*

must have crystallized above 91° C. and must contain at least 8 per cent. dissolved covellite; otherwise it would be orthorhombic and not isometric. Posnjak, Allen, and Merwin [13] also found that one sample of Kennecott chalcocite actually contained over 8 per cent. dissolved covellite, and concluded that it was in solid solution with the chalcocite. Thus there is careful experimental work which proves that solid solution between chalcocite and covellite does take place experimentally and that it occurs in the natural Kennecott ores.

The predominance of isometric chalcocite in the Kennecott ores indicates, therefore, that solid solution between chalcocite and covellite is the rule rather than the exception in this deposit.

"Diabasic" Covellite.—Bateman has pointed out [14] that among the various forms of chalcocite-covellite intergrowths found in the Kennecott ores there is a common and striking one that stands out in marked contrast to the microtexture so diagnostic of supergene covellite. This consists of acicular, or lath-like crystals of covel-

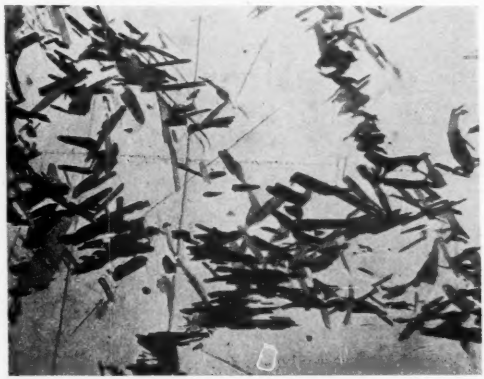


FIG. 1. Diabasic covellite. Laths of covellite (dark) in chalcocite (white), Kennecott. This type of covellite occurrence suggests natural unmixing from a solid solution of covellite in chalcocite. × 68.

[13] *Idem*, p. 510.

[14] Bateman, Alan M.: Some Covellite-Chalcocite Relationships, *op. cit.*, pp. 426–427.

lite imbedded in chalcocite, much resembling phenocrysts of feldspar in a diabase, hence its name (Figs. 1, 3).[15] They commonly have no relation to cracks or veinlets in the chalcocite and may be definitely oriented in a triangular pattern. These covellite laths are mostly of microscopic size and may be sparingly scattered in the chalcocite or be so abundant as to form a felted mass.

Under the microscope, in plane reflected light, the covellite laths range in color from white to a beautiful deep blue, depending upon the orientation of the crystals. Under crossed nicols they take on brilliant high colors which change with the rotation of the stage; they extinguish parallel to the cross-hairs. Consequently, there is a striking color contrast between the brilliant covellite and the somber chalcocite which enables the minerals to be distinguished at a glance. Even the slightest microscopic thread of covellite stands out so brilliantly under crossed nicols that there is not the slightest doubt as to the presence or absence of this mineral—a distinction the significance of which will be evident later. Some of the laths clearly outline octahedral partings in the chalcocite.

This is the variety of covellite whose origin is puzzling. Does it represent earlier crystallized covellite surrounded by later chalcocite, or replacement (either hypogene or supergene) of chalcocite by covellite, or simultaneous deposition? It was suspected previously that the pattern might be due to unmixing from solid solutions, and in the earlier experiments[16] this was verified. Gentle heating caused the covellite laths to disappear so that not a vestige of the startlingly brilliant covellite could be discovered. A similar structure was made to reappear upon slow cooling, although it could not be reproduced at will.

This type of intergrowth, therefore, suggests natural ex-solution of covellite and chalcocite.

Transition of Chalcocite to "Diabasic" Covellite.—A striking feature of the chalcocite-covellite relationships in the Kennecott ores is the transition from blue, and blue and white, chalcocite to "diabasic" covellite. Some of the stages are: (1) isometric blue chalcocite; (2) isometric blue and white chalcocite containing

[15] See also Fig. 1, Bateman, Alan M.: *Idem*, p. 427.

[16] *Idem.*

"invisible" covellite;[17] (3) crypto-covellite along parting planes in chalcocite;[17] (4) microscopically visible covellite in similar orientation; (5) larger blades of covellite that outline triangular octahedral partings in the chalcocite with locally developed groups of laths that spread out in miniature intergrowths; (6) "diabasic" intergrowths.

The chalcocite partings less commonly are outlined by fine blue lines that show no covellite but nevertheless display, under crossed nicols, a reddish hue which indicates that some covellite is present.

The crypto- and visible covellite along the octahedral parting planes of the chalcocite do not cross each other but either taper off or end toward their intersection; weaker laths may continue on the other side of stronger ones. This arrangement is in marked contrast to the joining and spreading of replacement veinlets at their intersection, a distinction pointed out by Geijer.[18]

Of these various transitions, the isometric blue, and blue and white, chalcocite indicate solid solution and the other stages suggest progressive steps of ex-solution.

"Eutectoid" Intergrowths.—Much of the isometric chalcocite of Kennecott is later than and replaces covellite. In some interesting specimens, bands of later chalcocite cut across massive covellite (Fig. 2). Within these bands are central lens-like areas containing covellite laths whose orientation shows no relation to that of the invaded covellite; on the contrary, they are oriented along the octahedral parting directions of the invading isometric chalcocite (Figs. 2, 3). The texture is "eutectoid." The remainder of the invading chalcocite is commonly the blue variety containing only a few sporadic laths of covellite.

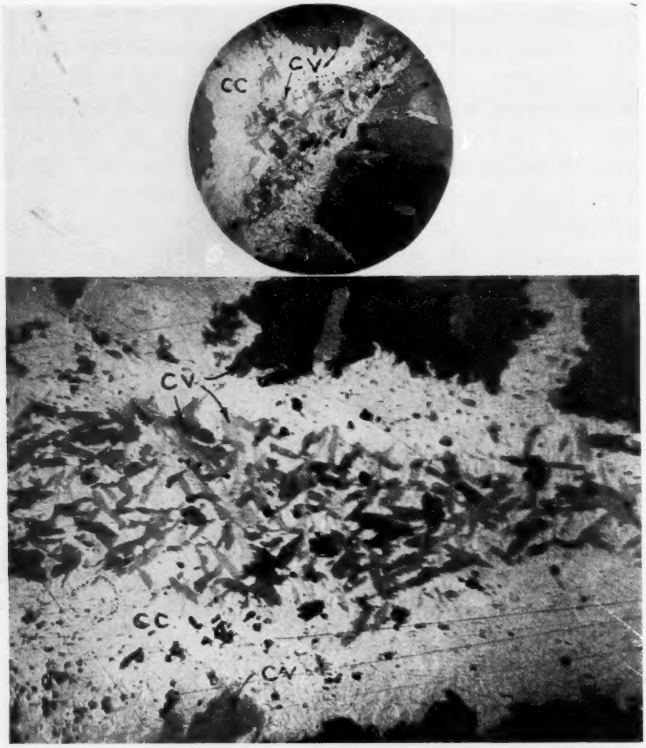
This relationship suggests that the later chalcocite (perhaps entering as a colloid) may have dissolved the covellite that it invaded, giving rise to a band of chalcocite heavily charged with dissolved covellite, and upon crystallization and cooling, the ex-

[17] This is determined by prolonged etching which removes the chalcocite, leaving covellite which becomes visible under crossed nicols.

[18] Geijer, Per.: Some Swedish Occurrences of Bornite and Chalcocite. Sver. Geol. Und., Ser. C. 321, Ars. 17, 2, pp. 42–43.

cess covellite separated out, perhaps as a "eutectoid," to form the core.

This interesting occurrence, therefore, indicates that a solid solution actually exists, and suggests that ex-solution may have



FIGS. 2 and 3. Veinlet of chalcocite (white) traversing and replacing coarsely crystalline covellite (dark). Kennecott. Fig. 2 (top), (×36). Fig. 3 (×94), an enlargement of Fig. 2 shows oriented blades of covellite within the same chalcocite veinlet. It is considered that the chalcocite dissolved the earlier border covellite, and later unmixing formed the second generation bladed covellite.

taken place. The possibility that the chalcocite could actually have dissolved the invaded covellite is supported by the earlier experiments which showed that solution could be induced in the solid state at temperatures as low as 75° C.[19]

Conclusions.—The several features enumerated above prove that actual solid solutions exist in the Kennecott ores. They also suggest strongly that unmixing may have taken place to give rise to some of the microtextures described. Natural occurrences, therefore, offer evidence of solid solution and ex-solution of chalcocite and covellite. Further support of this is to be found in the experiments to be described and in the following discussions. Other natural occurrences of solid solution and unmixing between minerals are of course well known. That of the feldspars is common knowledge and several others have previously been pointed out.[20]

PREVIOUS EVIDENCE OF SOLID SOLUTION OF CHALCOCITE AND COVELLITE.

Earlier Studies.—The early considerations of the possibility of solid solution between chalcocite and covellite have been reviewed by Posnjak, Allen, and Merwin,[21] who point out that Hittorff, as early as 1851, discovered that when copper and sulphur are fused together the product always contains more sulphur than should occur in cuprous sulphide. The phenomenon was repeatedly observed later and it was thought that the synthetic products contained some cupric sulphide, possibly in solid solution. Posnjak, Allen, and Merwin then carried on careful investigations of the subject. Their results supported the earlier work and in addition they discovered that some natural chalcocites [22] also contain an excess of sulphur over that necessary to satisfy the formula Cu_2S. They established, upon the basis of experimental work with synthetic sulphides, that the excess sulphur represents

[19] Bateman, Alan M.: Some Covellite-Chalcocite Relationships, *op. cit.*, p. 431.
[20] *Idem*, p. 425.
[21] *Op. cit.*, pp. 496–497.
[22] From Kennecott, Alaska, and Tularosa (Bent) district, New Mexico.

a solid solution of covellite in chalcocite. Their work will be discussed later.

A further mention of solid solution between chalcocite and covellite was made by Bateman and McLaughlin [23] in 1920, in which they referred to the co-existence of isometric and orthorhombic grains of chalcocite as possibly due to original differences in dissolved covellite. Also, Per Geijer,[24] in 1923, described the co-existence of grains that yield orthorhombic and isometric etch patterns in chalcocite at Kiirunavaara and at Lukavaara, Sweden, and advanced a similar explanation.

The Work of Posnjak, Allen, and Merwin.[25]—In their careful investigations, these workers recognized that covellite might be present in mechanical mixture with the chalcocite but concluded that this was not the case, one reason being that their synthetic chalcocite was microscopically homogeneous, although containing excess sulphur. It appears, however, that the application of the X-ray to crystal analysis has shown the criterion of microscopic homogeneity to be unsound, since cryptomicroscopic mechanical mixtures may exist.[26] However, their conclusion is adequately proved by the covellite dissociation curve of Preuner and Brockmoller,[27] which indicates that the existence of unchanged covellite at temperatures around 1000° C. would not be expected, as opposed to the fact that synthetic chalcocite contains about 1.4 per cent. excess sulphur even at the melting point, 1130°. In addition, their pure powdered covellite mechanically mixed with powdered chalcocite disappeared upon heating. The possibility that the excess sulphur was due to a solution of chalcocite and sulphur was also considered, but discarded in favor of the solution being covellite in chalcocite.

Posnjak, Allen, and Merwin then showed that increasing amounts of dissolved covellite gradually raise the inversion point

[23] *Op. cit.*

[24] *Op. cit.*, pp. 10 and 21.

[25] *Op. cit.*

[26] Kozu, S. and Endo, Y.: X-Ray Analysis of Adularia and Moonstone and the Influence of Temperature upon the Atomic Arrangement of Minerals. Sc. Rep., Tohoku Imp. Univ., Sendai, Japan, Ser. III. vol. 1, No. 1, June, 1921.

[27] Zeit. Phys. Chem., 81, 129, 1912.

of isometric to orthorhombic chalcocite from the normal at 91° C., to about 93.5° C. with 6 per cent. covellite and above 8 per cent. inversion is completely prevented (Fig. 4). They found that with increasing content of covellite their synthetic chalcocite be-

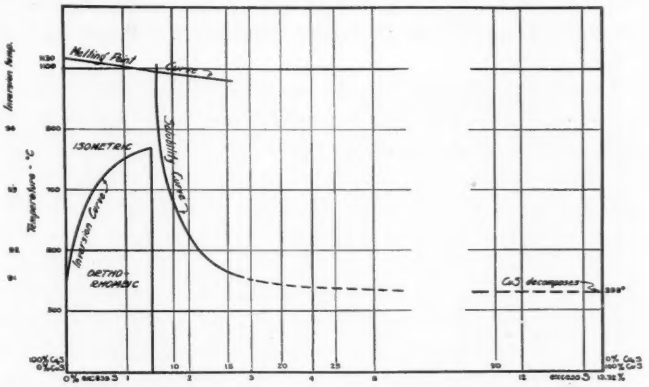


FIG. 4. Curve showing the effect of excess sulphur (dissolved CuS) on chalcocite. Adapted from Posnjak, Allen and Merwin.

came more and more blue, the inference being that this color was due to the dissolved covellite.

Fedotieff's Studies.—In 1927, Fedotieff [28] investigated the system $FeS.Cu_2S$ by methods of thermal analysis and found that by simple cooling of $FeS.Cu_2S$ melt, native copper separates from the system without the presence of any reducing agent. Upon re-melting, solution agãin takes place. His explanation is that the reversible equation $Cu_2S \rightleftarrows CuS + Cu$ takes place and that upon separation of copper a contemporaneous solid solution of $CuS.Cu_2S.FeS$ is formed. Fedotieff was aware of the work of Posnjak, Allen, and Merwin and of Friedrich and Waehlert,[29] which proved the stability of Cu_2S at temperatures even above the melting point, but even so, he considers the formation of

[28] Fedotieff, P. P.: Ueber die Ursache der Haarkupferbildung im Kupferstein. Zeit. f. Anorg. Chem., 167, pp. 329–340, 1927.

[29] Metall u. Erz, 1913, p. 977.

native copper in the binary melt as due to the instability of cuprous sulphide during cooling of its solid solution. Observations were confined to the separation of copper from the system $FeS.Cu_2S$ and were not extended to an investigation of Cu_2S alone. The range of temperature at which Fedotieff believes that decomposition takes place was not accurately determined but appears to be around 550° C.

Recent Experiments.—In the experiments previously referred to [30] it was found that in intergrowths of covellite and chalcocite the covellite laths disappeared with heating, and that a seemingly homogeneous surface resulted; the areas that were covellite answered every test for isometric chalcocite. No trace of covellite could be discerned by the delicate test under crossed nicols with reflected light. Presumably solid solution took place. A surprising feature was the low temperature at which the transformation took place. No change occurred at 50° C., but at 75° C. a few per cent. of covellite in chalcocite became dissolved in three hours; at 100° to 120° C. the covellite disappeared in one to two hours.

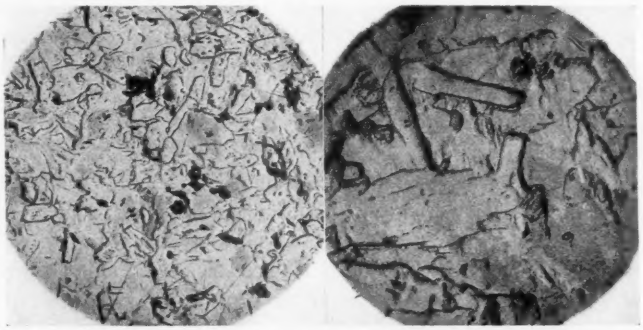
The disappearance of the covellite was attributed to solid solution; reasons were given [31] for considering that the covellite was not converted into chalcocite by driving off an atom of sulphur from the covellite. Pure covellite was not affected by the heat treatment and where it reached or exceeded 30 to 40 per cent. of the chalcocite present, solution was not complete; frayed remnants of covellite remained. Complete disappearance of covellite occurred only with a relatively small proportion of covellite to chalcocite, or with longer time. Some orthorhombic chalcocite with included covellite became isometric when heated above 91° C. This was one of the reasons for concluding that solid solution had taken place. A peculiar feature of the heated surface was that it possessed noteworthy relief; the area of each former covellite lath stood out in relief, indicating its original position and shape (Figs. 5, 6), but these areas tested for chalcocite, not covellite.

[30] Bateman, Alan M.: Some Covellite-Chalcocite Relationships. ECON. GEOL., vol. 24, pp. 424–439, 1929.

[31] *Idem*, p. 435.

Another feature was that solution appeared to take place in one direction only, i.e. covellite dissolved readily in chalcocite but no chalcocite appeared to dissolve in covellite, at least to a visible extent.

Attempts at unmixing were not so satisfactory. Some separation of covellite was brought about by slow annealing but this



5 6

FIG. 5. Chalcocite with inclusions of covellite, after heating, but not repolished. All lath-like inclusions of covellite have disappeared; residual frayed remnants (dark gray) of larger irregular grains of covellite still remain. Areas in relief are chalcocite that was covellite. × 40. (After Bateman, *op. cit.*, ECON. GEOL., vol. 24, p. 429.)

FIG. 6. Covellite inclusions in chalcocite after heating. Areas in relief were formerly covellite but are now changed to chalcocite. Faint darker areas are residual covellite grains only partly dissolved in the chalcocite. × 80. (After Bateman, *op. cit.*, ECON. GEOL., vol. 24, p. 429.)

result could not be induced at will. The controls were not established.

The experiments, however, indicated clearly that solid solution between natural intergrowths of chalcocite and covellite could be readily induced and that some unmixing could be brought about, yielding microtextures similar to those of natural intergrowths and suggesting thereby that the natural intergrowths had originated in a similar manner. They furthermore suggested a hypogene origin of ores that display similar intergrowths. But the

experiments also raised several interesting problems that demanded further investigation.

THEORETICAL CONSIDERATIONS.

Before carrying out further experiments on the solid solution of covellite and chalcocite, it seemed advisable to inquire into what is implied by "solid solution." So far as could be determined there are no natural analogies to which solid solution of covellite and chalcocite can be compared. Solid solutions are common, but not solid solutions in which one of the components of the solute is identical with the solvent. Pyrrhotite does not constitute a comparable case.[31a]

There is a difference between solution of covellite in chalcocite in the solid state, with later possible unmixing, and a union of colloidal chalcocite with adsorbed sulphur forming covellite that would be retained in solution by the excess chalcocite [32] but might, during or after crystallization of the chalcocite, unmix to form the natural intergrowths. Since the covellite laths occur along chalcocite parting directions, it would seem that unmixing takes place after crystallization.

In the latter case, covellite has been formed from chalcocite and sulphur, but whether the union took place at once and covellite existed as such within the chalcocite, or whether the chalcocite and sulphur retained their identities up to the point of unmixing, is unknown.

The former case is somewhat different. What becomes of the covellite as it disappears? Does it enter into the structure of the chalcocite as covellite? Does it break down into $Cu_2S + S$, with the sulphur going into solution in the chalcocite? Or does the suggestion of Fedotieff that chalcocite breaks down into covellite and copper have any bearing? The fact that the solute may readily be broken up into two parts, one of which is identical with

[31a] Posnjak, Allen, and Merwin: *op. cit.*, p. 512.

Allen, E. T., Crenshaw, J. L., and Johnson, J.: The Mineral Sulphides of Iron. Amer. Jour. Sci., vol. 33, pp. 169–236, 1912.

[32] See Lasky, S. G.: A Colloidal Origin of Some of the Kennecott Ore Minerals, ECON. GEOL., vol. 25, pp. 737–757, 1930.

the solvent, offers a third complication. Is it possible for the covellite that goes into solution to break up into Cu_2S and S ions, electrolitically charged, such as $2CuS = (Cu_2S)^{++}S^{--}$? This is a matter of which little is known; it has always been assumed that a mobile solution is necessary for ionization, yet new compounds do form from old by metamorphism, and ionic migration in solids is thus an implied process.

Fedotieff's suggestion may be dismissed for a number of reasons:

1. The work of Posnjak, Allen and Merwin, and of Friedrich and Waehlert, already cited, proves the stability of cuprous sulphide even at temperatures above the melting point.

2. In regard to reactions at lower temperatures, Posnjak, Allen and Merwin [33] make this statement: "With decrease in temperature and increase of sulphur vapor pressure the amount of sulphur in these sulphides increases and their composition lies within the limits of cuprous and cupric sulphides." Fedotieff did not investigate reactions of Cu_2S by itself, but confined his attention to, and drew his conclusions from, observed reactions in the presence of FeS.

3. The decomposition range, according to Fedotieff, is around 550° C. This is much higher than the temperatures at which observed reactions in our experiments take place, which are as low as 75° C.

Volume Change.—The apparent increase in volume of the areas that originally were covellite is rather surprising. The specific volume of covellite [34] is 0.2135; that of chalcocite is 0.1728; a reduction in volume is therefore indicated in the change of covellite into chalcocite. Further, inasmuch as two molecules of covellite are required to produce one of chalcocite, and since the chalcocite molecule is less in volume than one of the two covellite molecules, a still greater reduction is indicated. Consequently, in the change from covellite to chalcocite, depression rather than elevation should mark the former covellite sites.

[33] *Op. cit.*, p. 503.

[34] Using the specific gravity obtained at the Geophysical Laboratory.

The specific gravity of pure Cu_2S as determined at the Geophysical Laboratory is 5.802;[35] it is inferred that this applies to the orthorhombic form. Barth[36] has succeeded in measuring the cube of the isometric form at 200° C. and computes the specific gravity at that temperature to be 5.97. Since chalcocite with over 8 per cent. dissolved covellite, if heated above 91° C. is isometric, the high specific gravity obtained by Barth is another reason for expecting depressional areas rather than elevated ones, if solution involves the breaking up of covellite into chalcocite and sulphur.

The dissolved sulphur may, however, exert an internal pressure upon the members of the chalcocite lattice, and the consequent change in volume may balance or possibly exceed the normally expected reduction. Naturally, the manner of migration of the sulphur would affect such possible pressure. The sulphur atoms may occupy the interstices of the chalcocite lattice. Perhaps the sulphur lattice penetrates the chalcocite lattice or unites with it. In the latter case, the result would be $Cu_2S + S$ to form covellite, thus producing solution of chalcocite and covellite, not chalcocite and sulphur.

Disregarding the effect of the change of volume of chalcocite upon becoming isometric, 0.427 cc. of covellite should become 0.1728 cc. of chalcocite, a reduction of 60 per cent.; it is not to be expected that the pressure of dissolved sulphur can more than double the normal volume of chalcocite.

As has been mentioned, an increase and not a decrease of volume appears to take place. Specimens that have been heated show not only relief in the areas of former covellite but, in addition, the individual grains of the surrounding chalcocite appear to have been differentially elevated and tilted with respect to each other as if either expansion had forced them upward or contraction had permitted them to settle. Furthermore, the cleavage directions of the chalcocite become clearly outlined by ridges, suggestive that invisible covellite had been present along the part-

[35] *Op. cit.*, p. 505.

[36] Barth, T.: Die Reguläre Kristallart von Kupferglanz. *Centr. f. Min.*, 1926–A, p. 284.

ing planes and upon solution had given rise to relief similar to that exhibited by the visible covellite laths.

On the basis of the discordant volume changes it does not seem probable that solution takes place by the breaking up of the covellite into chalcocite and sulphur, even permitting the sulphur to remain in the system. Furthermore, the low temperature at which the changes take place also opposes the idea of an actual breakdown of covellite. The possible loss of sulphur from the system will be discussed later. The most probable explanation of the change, in the light of our knowledge to date, is that solution takes place by the covellite dissolving as such in the chalcocite. Theoretically there need not be a volume decrease. At its greatest, a possible reduction in volume would be insignificant as compared to that attending the conversion of covellite into chalcocite, and it is believed that it would be far outweighed by the pressure effect of the dissolved material, so that a volume increase would not be incompatible. This explanation on the whole closely fits observed experimental changes and is in agreement with the ideas of Posnjak, Allen and Merwin.

X-RAY EVIDENCE.

Some X-ray studies were undertaken in order to determine, if possible, whether isometric chalcocite shows a different pattern from that of the orthorhombic variety, and whether it might disclose the nature of the solid solution and the presence of covellite or sulphur in the isometric chalcocite. Covellite was also pictured to make sure it is normal covellite and for contrast with the chalcocites. It was intended to have X-ray pictures taken of the material that was covellite but upon heating became chalcocite. However, it proved impossible to obtain the necessary quantity, small though it is, because of a surprising disclosure that will be discussed later.

For the X-ray work and the accompanying diagram, tables, and discussion, the writers are indebted to Professor Paul F. Kerr of Columbia University.

Two samples of Kennecott covellite[87] were X-rayed. Both

[87] Collection Numbers Kn 56 and Kn 155.

of these yielded good patterns which agree with those taken of pure crystallized covellite from Alghen, Sardinia, and from Rio Grande, Colo. The covellite (Kn 56) contained by analysis 0.60 per cent. pyrite and a small amount of excess copper, but in regard to this Dr. Kerr states: "In case only a fraction of one per cent. excess copper is present, I doubt whether the X-ray pattern is sufficiently sensitive to disclose it." The covellite patterns (Fig. 7) and measurements (Table I) were compared with

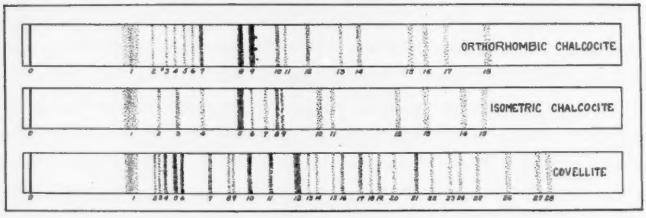


FIG. 7. Diagram illustrating the relative interplanal spacings of orthorhombic chalcocite, isometric chalcocite, and covellite. The numbers opposite each line agree with the system of numbering followed in Table I. (Drawn by Dr. Paul F. Kerr.)

similar patterns and measurements obtained by Roberts and Ksanda,[38] who used covellite from Summitville, Colo. and synthetic covellite, both of which gave identical results.

Three samples of isometric chalcocite[39] were X-rayed, giving identical patterns. For comparison, two specimens of Kennecott orthorhombic chalcocite[40] were X-rayed and check patterns were obtained from other orthorhombic chalcocites from Messina, Transvaal (Afr. 713a), Bristol, Conn., and Globe, Ariz. (See Fig. 7 and Table I.) Dr. Kerr states:[41] "The covellite yields satisfactory X-ray diffraction patterns. The two varieties of chalcocite, however, fail to produce as well developed and as numerous lines. A maximum of eleven lines represents the best

[38] Amer. Jour. Sci., (3) XVII, pp. 489–503, 1929.
[39] Collection Numbers Kn 7, Kn 83.2, Kn 107.
[40] Collection Numbers Kn 83, Kn 173.
[41] Letter, Feb. 20, 1931.

chalcocite pattern secured. The lines that are developed, on the other hand, show a difference easily recognized between orthorhombic and isometric chalcocite."

TABLE 1.

X-RAY DIFFRACTION MEASUREMENTS OF ORTHORHOMBIC CHALCOCITE, ISOMETRIC CHALCOCITE AND COVELLITE (BY KERR)

Orthorhombic Chalcocite.		Isometric Chalcocite.		Covellite.		
Line No.	Interplanar Spacing in Å.	Line No.	Interplanar Spacing in Å.	Line No.	Interplanar Spacing in Å.	Form.†
1	3.89 (diffuse)	1	3.93 (diffuse)	1	3.88 (diffuse)	
2	3.39 f	2	3.22 f	2	3.33 f	$(10\bar{1}0)$
3	3.04 f	3	2.80 m	3	3.24 f	$(10\bar{1}1)$
4	2.87 f	4	2.41 ff	4	3.07 s	$(10\bar{1}2)$
5	2.69 f	5	1.975 sss	5	2.84 sss	$(10\bar{1}3)$
6	2.56 f	6	1.880 f	6	2.74 s	$(00\bar{0}6)$
7	2.42 sss	7	1.765 f	7	2.31 f	$(10\bar{1}5)$
8	1.96 sss	8	1.685 m	8	2.09 ff	$(10\bar{1}6)$
9	1.87 sss	9	1.516 f	9	2.05 ff	(0008)
10	1.77 s	10	1.445 ff	10	1.895 sss	$(11\bar{2}0)$
11	1.64 f	11	1.335 ff	11	1.740 ss	$(10\bar{1}8)$
12	1.505 m	12	1.140 m	12*	1.555 sss	$(11\bar{2}6)$
13	1.350 f	13	1.076 ff	13	1.515 fff	$(20\bar{2}4)$
14	1.275 m	14	.977 ff	14	1.465 ff	$(20\bar{2}5)$
15	1.110 f	15	.938 ff	15	1.380 f	$(20\bar{2}6)$
16	1.065 f			16	1.345 f	$(20\bar{2}7)$
17	1.017 f			17	1.270 f	$(20\bar{2}8)$
18	.930 f			18	1.240 ff	$(12\bar{3}2)$
				19	1.210 f	$(12\bar{3}3)$
				20	1.160 ff	$(12\bar{3}5)$
				21	1.090 m	$(30\bar{3}0)$
				22	1.055 f	
				23	1.010 f	
				24	.987 f	
				25	.950 ff	
				26	.893 ff	
				27	.843 ff	
				28	.827 ff	

Intensity of lines:

sss = strongest.
ss = moderately strong.
s = strong.
m = medium.
f = faint.
ff = very faint.
fff = faintest

* Possibly a double line, $20\bar{3}3$ may be obscured.

† The form indices in this column are after Roberts and Ksanda.

Dr. Kerr further states:[42]

Line No. 1 in the pattern for covellite was not reported by Roberts and Ksanda, although a diffuse line corresponding to a spacing of about

[42] *Idem.*

3.88 angstrom units has been found in all the patterns of covellite recently secured. A single diffuse line appears likewise in the case of orthorhombic and isometric chalcocite. The diffuse line is in approximately the same position occupied by a rather strong doublet in the X-ray diffraction pattern of orthorhombic sulphur. It might be suggested, therefore, that line No. 1 in each pattern is possibly due to the presence of free sulphur. The amount of reliance to be placed on this interpretation, however, should depend upon the extent to which it agrees with parallel chemical studies.

Unfortunately the lack in intensity in the lines secured in the X-ray diffraction patterns of both orthorhombic and isometric chalcocite makes the attempt at any assignment of crystal structure hazardous until better patterns can be secured. Comparison of the measurements of the lines for isometric chalcocite with the chart for isometric crystals furnished by Hilger shows agreement with an isometric structure.

The lines in the pattern of isometric chalcocite that appear to distinguish it from orthorhombic do not match any of the prominent lines of covellite. For that reason it appears to me that it is in all probability due to a difference in structure. On the other hand, a small percentage of covellite in chalcocite, even enough to make the isometric form possible, might easily escape detection in the X-ray diffraction patterns. Also the isometric chalcocite contains fewer lines than the orthorhombic chalcocite, suggesting further that the pattern is not a mixture of chalcocite and covellite.

Fig. 7 presents a graphic plot of the relative intensities and positions of the various lines for patterns of orthorhombic chalcocite, isometric chalcocite, and covellite.

It is probable that, aside from lines due to possible traces of sulphur (No. 1), the lines may all be assigned to the various minerals represented. That is, it does not seem likely that the patterns represent mineral mixtures. In the case of isometric chalcocite, for instance, lines due to covellite appear to be absent. This may be explained by the common lack of sensitivity on the part of X-ray diffraction patterns to small amounts of impurity.

From Dr. Kerr's statements, figure, and table, it is clear that orthorhombic and isometric chalcocite can be distinguished by means of X-rays, also that the isometric variety does not appear to be a mixture with covellite. It is likewise clear that the nature of the solid solution that gives rise to isometric chalcocite is not revealed by X-rays; there is a suggestion, only, that free sulphur may be present in the minerals.

Further Experimental Data.

Extent of Solid Solution.—A surprising feature of the change attending solid solution was accidentally encountered, and no adequate explanation can as yet be offered. A specimen which, upon the polished surface, showed nearly complete solution of the covellite, was sawn in two with the intention of preserving one half and annealing the other to obtain unmixing. It was noted that on the cut surface the covellite within the center of the mass had apparently not been dissolved. The original surface was then reground with the result that covellite was found under a relatively thin layer. The appearance of covellite upon the cut surface was, therefore, not due to any effect produced during the sawing operation.

The repolished surface was again heated but only a fraction of the covellite dissolved; it was repolished and heated a third time, with the result that no solution took place. A number of other specimens were treated in a similar manner and it was found that in every case, regardless of the amount of covellite originally present, solid solution took place to only a thin depth. The entire mass also apparently suffered some change that prevented solution of the subsurface covellite even after it was brought to the surface by polishing. Heating at temperatures as high as even 300° C. yielded the same results. One specimen was carefully weighed before heating and after repolishing, and the area of the surface was measured. From these data (subject to errors, of course) it was computed that the depth of the film in which solid solution took place was less than 0.015 mm.

Some of the specimens used in the earlier experiments were reinvestigated and they likewise showed but a thin surface effect. In one specimen the film was much thicker but continued re-surfacing disclosed covellite beneath. It was at first considered possible that unmixing had taken place within the heart of the mass, but specimens quenched immediately upon withdrawal from the furnace were similar to the others.

Mutual Solubility of Chalcocite and Covellite.—It was found previously that areas of covellite changed over, upon heating, into

chalcocite, but that areas of chalcocite never changed over to covellite. This meant that solution had taken place, at least in large part, in only one direction. This point was investigated further to determine if at least a small amount of chalcocite may dissolve in covellite.

Schwartz[42] found a similar one-directional solution with bornite and chalcocite; he was unable to cause a small amount of chalcocite to dissolve in bornite; the bornite always disappeared into the chalcocite.

A careful analysis was made of a piece of covellite that was also X-rayed. It shows: Cu 66.19 per cent.; Fe 0.28 per cent (a trace of pyrite was visible), and S (by difference) 33.53 per cent. To form the pyrite known to be present, the 0.28 per cent. of iron would require 0.32 per cent. S. There would be left 33.21 per cent. of sulphur available for covellite consuming 65.87 per cent. copper. There is therefore 0.32 per cent. copper in excess of that necessary to form covellite. The excess copper would be equivalent to 0.48 per cent. dissolved cuprous sulphide. If the assumptions regarding the amount and disposition of the sulphur are correct, it would indicate that the covellite contains only a trace of chalcocite. The reaction is thus one sided—the covellite always changes into a mineral that answers all mineralographic tests for chalcocite.

A third piece of the nearly pure covellite that had been analyzed was heated at about 300° C. for 1½ hours. The temperature control may not have been precise but it is certain that the maximum temperature did not reach within 40° of the decomposition temperature of covellite, the lower limit of which, according to Posnjak, Allen and Merwin, is 358° C. Upon withdrawal from the furnace, the surface had to be lightly buffed to permit microscopic examination. The appearance yielded a surprise. What had originally been a homogeneous surface of covellite now presented a peculiar mottled appearance due to the presence of considerable "chalcocite"; about half the covellite had changed to "chalcocite." The appearance is one of replacement by chal-

[42] *Op. cit.*

cocite acting centrifugally from cores in individual laths of covellite, and also as invading veinlets. Contacts between this "chalcocite" and covellite are sharp; no pore space has been developed.

This particular change is not understood, since no sulphur has been driven from the system, and the covellite does not contain sufficient dissolved chalcocite to unmix as free chalcocite.

TEMPERATURE OF SOLUTION.

The earlier experiments established a surprisingly low solution temperature.[44] Temperatures above 150° C. were found unnecessary, and a few hours of heating proved as effective as a few days. A temperature of 50° C. was found too low but one specimen showed solid solution at 75° in three hours. The temperature at which solution begins was therefore referred to between 50° and 75° C. It was decided to determine this solution temperature within narrower limits. Accordingly, a duplicate of the last-mentioned specimen was subjected to gradually increasing temperature, beginning at 55° C. and raised by 5° increments, at 18-hour intervals. The specimen was examined every few hours. No solution took place at the lower ranges but three hours of heating at 60° developed excellent octahedral parting in the chalcocite. At 70° there was no sign of solution but after two hours of heating at 75° the edges of the covellite laths were beginning to take on a grayish color. Some laths were hardly affected; the smaller ones were almost completely changed. There was no indication of relief. After another 20 minutes, the fading had become more widespread; pleochroism became fainter; the covellite revealed a pepper-and-salt mottling and relief appeared. Thus relief starts before solution becomes complete. After three hours of heating, the partings that had previously developed within the chalcocite became narrow ridges, suggesting that the chalcocite had contained invisible unmixed covellite along the parting planes. A trace of undissolved covellite still remained, even after 24 hours of heating; a trace even persisted after three hours at 77°. Octahedral partings stood out in prominence by "solution ridges."

[44] Bateman, Alan M.: Some Covellite-Chalcocite Relationships, *op. cit.*, p. 431.

Solution thus takes place within a temperature range of 5°; none occurred at 70°; it took place readily at 75° C.

POSSIBLE LOSS OF SULPHUR.

Whether solution took place by the breakdown of covellite into chalcocite and sulphur, or by migration of ions, or by diffusion of each into the other, has already been discussed. It has been shown that the first does not appear probable, even assuming that the sulphur would remain within the system. The possible loss of sulphur from the system was then further investigated.

Several specimens were heated in boiling water until maximum solution had occurred; the water gave no test for either S^{--} or SO_4^{--}, even after boiling down to small volume in order to concentrate any dissolved material.

Pure covellite showed no change when heated up to 175° C. At higher temperatures, however, striking changes occurred. A specimen of pure covellite [45] was placed in an electric furnace together with two others that consisted of about equal quantities of covellite and chalcocite, and heated gradually to 325° C. One of the specimens with chalcocite was the same one that showed no solution upon reheating after the initial surface solution film had been removed; the other was a fresh specimen of the same material.. The temperature was inadvertently permitted to rise to 360° for about ten minutes; suddenly, the covellite specimen exploded violently. It will be recalled that it was determined at the Geophysical Laboratory that covellite loses its sulphur above 358° C. The specimens with chalcocite in them, on the other hand, did not explode. Some of the covellite had disappeared into the chalcocite and both specimens became porous and pumice-like on the surface—proof that sulphur had been driven off. The pre-heated specimen appeared much more porous than the other. In this same heat run, there was also a specimen containing about 80 per cent. covellite; it likewise escaped sudden disintegration. The surface showed complete disappearance of the covellite.

[45] It was this so-called pure covellite that had been analyzed and found to contain 0.48 per cent. chalcocite.

Duplicate specimens of pure covellite and of that containing 50 per cent. chalcocite were subjected to a temperature of 500°. After only about ten minutes a loud report was heard; the covellite had exploded. This temperature was retained, however, for two hours in order to note the effect on the specimens containing chalcocite. When the furnace was opened and air entered, the powdered remains of the covellite specimen burst into a blue flame and a strong odor of SO_2 was apparent. The other specimen was found to be entirely changed to chalcocite; no trace of covellite was observed even within the core. The core was quite porous, as if a reduction of volume had taken place upon the conversion of covellite to chalcocite.

The violent breakdown of the pure covellite into chalcocite and sulphur was probably due to the generation of sulphur within the heart of the specimen, that could find no exit except by explosion. Where chalcocite was present, the reaction took place quietly. In no case was porosity produced commensurate in amount with the change.

A third set of specimens, identical with the above, were heated at 300° C. for 1½ hours. The one with 50 per cent. chalcocite showed the same effects produced on others at lower temperatures, *i.e.* solution of the covellite, attended by relief of the covellite areas, to a very thin depth. In the heart of the specimen is recrystallized covellite, surrounded by a zone in which about half of the covellite had been converted to "chalcocite," giving a peculiar mottled appearance. This specimen offers perhaps the best proof that pure covellite does not break down into chalcocite and sulphur at temperatures below 358°. The contacts between covellite and "chalcocite" are sharp; there is no evidence of sulphur; nor is there more than normal covellite porosity.

The specimen weighed 20 grams. To change 10 grams of this into chalcocite would involve a release of about 1.6 grams of sulphur, a quantity great enough to be detected readily if it were present. None was recognized.

The lack of induced porosity seems sufficient proof that no sulphur was driven off. The molecular volume of covellite is

20.36. Half of this, 10.18 cc., is equivalent to 47.815 grams, which by loss of sulphur would be converted into 39.80 grams of chalcocite, occupying 6.86 cc. Thus 10.18 cc. of covellite would be converted into 6.86 cc. of chalcocite, that is, a porosity of 3.32 cc. would be produced, equal to 16.3 per cent. The specimen experimented with has been half changed to "chalcocite," but it shows no increase in porosity, certainly none commensurate with the above figures. The obvious explanation of the phenomena is that no sulphur has been lost from the system and that the change may be only an apparent one.

The best evidence, however, that sulphur has not been lost from the system when the covellite changes to chalcocite, is that the solid solution of chalcocite and covellite, as will be shown later, unmixes again to yield covellite.

UNMIXING.

General.—A feature of the earlier experiments was the inability to obtain unmixing at will. After two unsuccessful attempts in the later experiments, by annealing in water from boiling to room temperature, and by annealing in calcium sulphide in water for 64 hours at 50°, it became clear that only by accident had the unmixed covellite been obtained in the earlier experiments. Consequently, it became evident that slow under-cooling from the solution temperature with appreciable retention in the upper portion of what Tammann [46] calls the labile zone, would be required. According to Tammann, crystallization begins at the freezing point of a substance, which in this case may be considered the solution temperature of covellite in chalcocite, but the rate is at first extremely slow, rising rapidly to a maximum, and thereafter just as rapidly declining. The number of centers of crystallization, as well as the linear crystallization velocity, depends upon the temperature of under-cooling. The maximum velocity of crystallization growth lies at a temperature above that which promotes crystallization from a maximum number of centers, and "between these two temperatures the conditions are more favor-

[46] Tammann-Mehl: The States of Aggregation, Chap. 9. New York, 1925.

able for the formation and growth of crystallization than they are outside of the temperature interval" (Fig. 8). The number of crystallization nuclei formed in a given under-cooling is also a function of the temperature that has been applied *before* under-cooling. The higher the temperature preceding under-cooling,

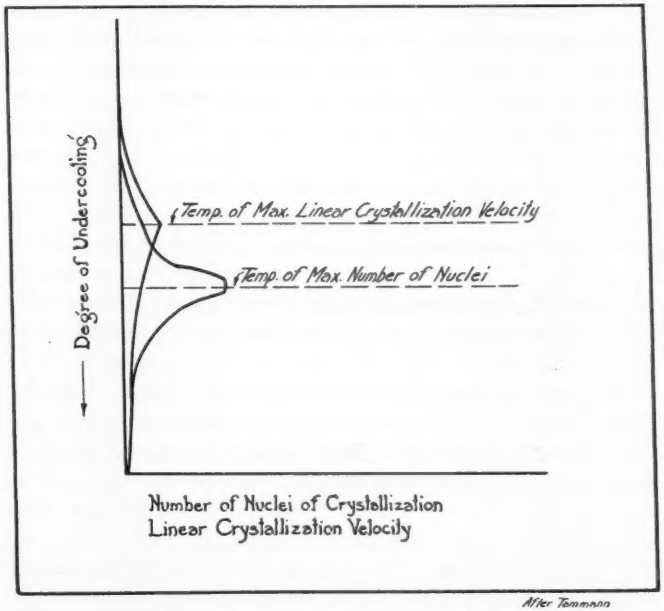

Degree of Undercooling
Temp. of Max. Linear Crystallization Velocity
Temp. of Max. Number of Nuclei
Number of Nuclei of Crystallization
Linear Crystallization Velocity
After Tammann

FIG. 8. Curve illustrating the dependence of linear crystallization velocity and the tendency toward spontaneous crystallization upon the temperature of undercooling. After Tammann.

the smaller the number of nuclei that will be formed. The rate of growth and the number of centers are likewise a function of the length of time that under-cooling is applied within a given range.

Tammann's observations apply to solid solutions as well as to liquids. Rose [47] says with respect to the annealing properties of

[47] Rose, T. K.: On the Annealing of Coinage Alloys. Jour. Inst. of Metals, vol. 8, pp. 86–125, 1912.

a variety of coinage alloys: "The annealing action at any given temperature is most active at first and gradually dies away . . .; *a few minutes at such a temperature cannot be replaced, for practical purposes, even by hours of annealing at much lower temperatures.*[48]

Experiments.—Since excess pre-temperature retards recrystallization and unmixing, and since the most favorable "temperature interval" of Tammann cannot, with low temperatures, be far below the solution point, under-cooling experiments were started at a temperature just below the determined solution point, which was found to lie between 70° and 75°. As the entire unmixing range lies above 50°,[49] it was decided that sufficiently slow under-cooling over a 5° range would maintain conditions in that zone between the two maxima in which crystallization takes place from the greatest number of centers compatible with high growth velocity. If unmixing takes place under such conditions a few easily visible crystals should form instead of a multitude of invisibly small ones.

The same specimen used to determine the solution point was reheated at 75° for 12 hours in order to bring the dissolved covellite and its imprisoning chalcocite into a state of mobility equal to that at which solution takes place. Thereafter, the temperature was lowered at the rate of three-fourths of a degree every 12 hours, down to 66°. At the end of six days the specimen was found to contain about 5 per cent. covellite that had unmixed in needle-like crystals clearly visible at the low magnification of 34. Under higher magnifications the appearance strikingly resembles some natural covellite-chalcocite intergrowths. (Compare Figs. 9 and 10 with Fig. 1.) The covellite separated along the chalcocite cleavages in long, slender crystals, forming triangular interspaces. Every stage of ex-solution was exhibited and the steps reverse those of solution. At first, there appeared a few scattered blue specks rudely aligned in the chalcocite; under crossed nicols these faint separations form zones of anisotropism. Next appear lath-like, non-pleochroic, gray-blue areas in which, as ex-solution

[48] The italics are ours.

[49] Previous experiments did not reveal unmixing by holding at 50° for 64 hours.

continues, blue spots in "pepper-and-salt" pattern make their appearance attended by slight pleochroism and the beginning of the normal extinction reds of covellite. The final appearance is of long, slender, clearly outlined blue crystals that appear to be normal in all respects. Most of the relief had disappeared. The new crystals occupy places irrespective of the position of the former covellite laths. Presumably, they grew at the expense of the covellite that had previously become dissolved. The regrowth of the covellite presumably removed the internal pressure that had previously caused the relief, and the elevated areas of former covellite returned to a microscopically smooth surface. The residual areas of relief mark the cleavage pattern of chalcocite, a further proof that parting planes (planes of weakness) tend to be the natural habitat of material on the verge of either solution or ex-solution.

The unmixed crystals of covellite do not cross each other; they continue their growth until another crystal is encountered, when one of them stops and the other continues. Commonly the crystals taper at their junctions. This description resembles that of the natural intergrowths previously described, and bears out Per Geijer's contention [50] that such a structure is characteristic of unmixing and may be used to distinguish unmixing from replacement.

To show that unmixing can be brought about in other kinds of chalcocite, a specimen of secondary chalcocite and covellite from Bisbee, Arizona, was subjected to similar heat treatment with equally successful results. The covellite unmixed in minute needles that lie parallel to the orthorhombic parting of the chalcocite.

Reference to Natural Minerals.—It has been pointed out earlier in this article that solid solution between chalcocite and covellite does take place and that it occurs in the natural Kennecott ores. Likewise, it has been demonstrated experimentally that unmixing of induced solid solutions in natural minerals has taken place. The resemblance between these artificial products of unmixing

[50] *Op. cit.*

(Figs. 9, 10) and natural intergrowths in the Kennecott ores (Fig. 1) must be more than fortuitous. The conclusion seems inescapable that certain types of intergrowths between chalcocite and covellite in the Kennecott ores must have resulted from unmixing by slow under-cooling during geologic time.

9 10

FIGS. 9 (left) and 10 (right). Chalcocite-covellite intergrowths produced in the laboratory by unmixing from solid solutions that were made by heating natural intergrowths of chalcocite and covellite such as Figs. 1, 3. The narrow ridges represent residual areas of relief that outline octahedral parting in the chalcocite. Before unmixing, these surfaces were similar in appearance to those shown in Figs. 5 and 6. × 39.

One particular specimen (Figs. 2, 3) is illuminating in this connection. A veinlet of chalcocite traverses coarsely bladed covellite against which it lies with irregular replacement boundaries. Along the central part of the chalcocite veinlet are scattered laths of covellite. Their arrangement bears no relation to the invaded covellite; rather they seem to lie along the octahedral parting planes of the chalcocite. Consequently most of the covellite must have remained in solution until the chalcocite had crystallized. The chalcocite between the central band of covellite laths and the invaded covellite walls is relatively free from covellite laths and is blue isometric chalcocite.

The interpretation is that the invading chalcocite dissolved to capacity the earlier covellite, forming a solid solution. Subsequent slow cooling caused unmixing of excess covellite, giving rise to the oriented covellite laths imbedded in the chalcocite. Some covellite still remained in solution, causing the chalcocite to be blue in color and preventing its inversion so that it has persisted in the isometric form. The central part of the chalcocite veinlet may conceivably be considered as a "eutectoid" intergrowth. Assuming a colloidal origin, the component parts are solid; the solutions were merely mechanical carriers and otherwise do not enter into this phase. If the invading chalcocite had been deposited as a gel, as seems likely, solution of covellite would probably have gone on readily and unmixing must have followed upon slowly lowering temperature. It seems probable, therefore, that this type of microtexture represents unmixed covellite and is not due to subsequent introduction of covellite by replacement of chalcocite.

Although replacement of covellite by chalcocite is common, the replacement front is quite distinct from the frayed, gnawed border of covellite that has been partly dissolved by chalcocite in the solid state. These frayed outlines, together with other features typical of incomplete solid solution, are entirely lacking in natural intergrowths. It is clear that solid solution has not taken place by a local rise in temperature subsequent to the crystallization of the minerals. The solid solution must have occurred at the time of original deposition, and a study of the Kennecott ores suggests two separate modes of formation for natural solid solutions: (1) the formation of solid solution by crystallization of (colloidal) chalcocite with adsorbed sulphur; and (2) by chalcocite (probably in a gel state) dissolving earlier-formed covellite. The processes might be explained as follows: For the first mode of formation, the sulphides that make up the Kennecott ores may have been transported in a highly dispersed condition [51] and flocculated upon reaching the limestone. Chalcocite and sulphur were always present; the sulphur likewise was highly dispersed

[51] Lasky, S. G., *op. cit.*, pp. 737–757.

but in a fluctual though gradually diminishing supply. Since the chalcocite is isometric, there must have been sufficient adsorbed sulphur to form the necessary eight per cent. covellite to prevent the inversion of the chalcocite. As the supply of sulphur gradually failed, decreasing accounts of covellite would be formed. Below a certain limit, controlled by the solubility of covellite in chalcocite, the covellite would not separate by diffusion, but would remain in solid solution to unmix later under the proper conditions.

The second mode of formation gives rise to the "eutectoid" microtexture previously described, and shown in Figs. 2 and 3. Chalcocite (gel) that may penetrate covellite at an elevated temperature and replace it, does not do so by ordinary metasomatic processes but by actually dissolving the covellite—a conclusion that seems unavoidable in the light of the laboratory results that show how readily covellite may be dissolved, and the highly suggestive natural intergrowths.

SUMMARY AND CONCLUSIONS.

Chalcocite and covellite form solid solutions within a few hours at the surprisingly low temperature of 70 to 75°; unmixing of the covellite is readily brought about by slow under-cooling within a narrow range below this temperature. For example, under-cooling within a range of 9° for only six days sufficed to cause the unmixing of numerous covellite crystals visible with low magnification. The growth of the new covellite crystals takes place irrespective of the position of the previous covellite, but always along parting planes of the chalcocite; maximum growth takes place parallel to the partings.

The solution is apparently only a one-way reaction; covellite dissolves readily in chalcocite, but only a trace of chalcocite, if any, dissolves in covellite.

The solution, experimentally, appears to be a film phenomenon.

No loss of sulphur takes place from the system at any temperature below the decomposition point of covellite; if appreciable chalcocite is present, little loss occurs even at higher temperatures.

The physical changes that occur suggest that the solid solution of the covellite takes place by solution of the covellite as such. although the mechanics of the process is at present not known. It has been shown that sulphur does not leave the system and, because of the volume changes attending solution, it likewise seems improbable that covellite breaks down into chalcocite and sulphur with solution of the sulphur. Ionic migration is not impossible.

Since solution and ex-solution can be produced so readily, it seems probable that natural solutions occur and that many natural chalcocite-covellite intergrowths have been formed by unmixing. It is shown that most of the Kennecott chalcocite is isometric and therefore the high temperature form; that it is in large part a natural solid solution with covellite. It is our belief that some of the Kennecott intergrowths of covellite and chalcocite have been formed by such unmixing. Consequently, such intergrowths represent a new group of micro-textures. The solution temperature of 70 to 75° is well above that of supergene processes, and unmixing, if it can be proved, constitutes a criterion of hypogene chalcocite. If the unmixing interpretation of the Kennecott ores is correct, this is another proof of the hypogene character of the Kennecott chalcocite, although this origin is amply demonstrated by the isometric character of the chalcocite and other features. If ex-solution can be proved for intergrowths that show orthorhombic chalcocite, the temperature of formation of the deposits can then be fixed between the limits of 70° and 93°.

The natural solid solutions in the Kennecott ores may be readily explained, it is thought, if the colloidal origin advanced for them is the correct interpretation. From such colloidal solutions, unmixing is to be expected during the geologic interval of slow cooling in which the temperature remains in the labile zone of crystal formation.

The small percentage of excess sulphur in otherwise pure covellite raises the question as to what is natural covellite and what is chalcocite. Apparently there may be all gradations in nature from pure chalcocite and covellite to solutions of the two within

a wide range of proportions, and to covellite containing excess sulphur, either in solution or mechanically admixed. Perhaps what are called chalcocite and covellite are not stoichiometric minerals but may be anything within the outlined limits.

ACKNOWLEDGMENTS.

The writers wish to acknowledge with thanks their indebtedness to Professor Paul F. Kerr of Columbia University for taking and interpreting the X-ray photographs; to Mr. F. C. Bond of the Colorado School of Mines for chemical analyses; to Professor A. Phillips of the Yale Hammond Laboratory for the use of equipment; and to Professors W. E. Ford, Adolph Knopf, and H. W. Foote, of Yale University, with whom some points of the problem were discussed.

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VEIN FILLING DURING THE OPENING OF FISSURES.[1]

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In the last ten years there have been many attempts among American mining geologists to clear up the mechanics of opening and filling of fissure veins. Spurr tried to solve the problem by assuming a magmatic consistency in the ores entering the fissures. Taber laid much emphasis on the force of crystallization exerted by the growing particles of the vein material; and in a new paper, Wandke [2] sought the way out of the problems presented in some veins at Guanajuato, Mexico,[3] by referring to the pressure of ore-bearing solutions, a process considerably discussed among American geologists in recent years. All authors agree that there is always some effect of metasomatism, but they differ widely in the degree of metasomatosis that must be assumed to fit the individual case of irregularity in vein filling.

To begin first with Wandke's assumption. I agree in the possibility of a large pressure on the walls, if there is no opportunity for the solution to escape from the open fissure. But, if the solution remains in the fissure, only a part of the open fissure can be filled by ore or vein material, corresponding to the percentage of material dissolved in the vein-forming thermal waters. An open fissure filled with stagnant solution can never be filled entirely by vein material.

On the other hand, if the solutions are not stagnant, but flowing (as in the passage upward from the parent magma to the earth's surface), they are constantly renewed and new material is brought up until the open space is filled entirely, or nearly so, by ore and gangue. But if the solutions are flowing, their pressure

[1] The original manuscript has been re-written by the editors.

[2] A. I. M. E. Tech. Pub. No. 342, 1930.

[3] Wandke, A., and Martinez, J.: The Guanajuato Mining District, Mexico. Econ. Geol., vol. 23, pp. 1–44, 1928.

on the walls, made up of the weight of the water column above, plus the friction head, is in most cases insufficient to struggle against the weight of the hanging wall until all the open space is filled by vein material; for the velocity of flow necessary to produce the necessary pressures is inconceivably high.

In reviewing the literature, I find a certain feature underemphasized. This is the movement of the fissure walls during the vein filling. C. D. Hulin [4] and others have described the repeated filling of small fissures produced by " intermineralization fault movements " but they lay too much emphasis on the entire brecciation of older vein filling material and recementation by later minerals. I believe that vein filling during the opening of fissures can be proved nearly everywhere and that the opening and filling of fissures at different periods rarely if ever happened in the formation of fissure veins. Since open fissures can exist only in a region where the geodynamic forces exert a tension on the rock, the movement of the walls results in an opening of cracks and fissures. As soon as there is any possibility for the solutions to force their way up from the parent magma through such a system of cracks, the flow begins, crystallization of vein material is initiated and, in a short time, the cracks are filled and closed by ore or gangue. Similar action, no doubt, occurs in crystallization from waters percolating downward from the zone of weathering.

The resultant structure of the fissure vein depends on whether the process of opening is slower or quicker than the filling by vein material. Should a large fissure open up quickly, the solutions can deposit their material only as layers on the walls. These layers begin to form during the opening; but because opening is quicker than crystallization, there is always a medial open space, suggesting, for example, in a 20-foot vein, two successive steps, as follows: (1) the opening of a fissure 20 feet wide; (2) its filling by vein material. Authors assuming these two steps in various districts, ask how a flat-lying or inclined fissure could have remained open until it was filled. In explanation, the " force of crystallization " or an " ore magma " is

[4] Hulin, C. D.: Structural Control of Ore Deposition. ECON. GEOL., vol. 24, pp. 15–49, 1929.

assumed to have opened the fissure. The hypothesis of ore magma intrusion is especially likely to be used, if the texture of the vein filling is massive. However, we know that massive texture can result from an original crystallization from solution, or from a later recrystallization of a formerly banded ore, and from the replacement of an earlier vein filling by later solutions percolating either upward or downward, "*i.e.* interior vein metasomatosis," ("innere Gang-metasomatose"; Krusch).

If opening is faster than filling, and if there is a large space in the middle of the open fissure, the hanging wall is no longer supported. It breaks down and then the fragments rest on the products of crystallization which have already been deposited on the footwall. "Unsupported fragments" then are no longer a problem but a simple proof of disturbance during the vein filling. They seem a little strange but in reality are not so, when they lie amidst a massive gangue.

Moreover, if the fragments breaking down from the walls of a fissure during the filling of the open space are parts of older crystallization, the structure becomes "brecciated."

Among the illustrations in Wandke's paper, I find three fragments broken down in time of fast opening. Fig. 1 (Wandke's Fig. 4) shows a fragment that has simply fallen at the beginning of the vein filling and therefore is coated with all the four sequent crystallizations that followed each other in this vein: white quartz, amethyst, blue chalcedonic quartz, vuggy quartz. My understanding of Fig. 2 (Wandke's Fig. 5) is opposite to that of Mr. Wandke. I believe that the fissure, during the crystallization of the amethyst, may not have been much broader than the double amethyst coatings themselves, and at one spot, the amethyst coatings from either side became continuous and fastened the hanging wall to the footwall. The fissure continued to open. At any other spot the movement resulted only in an enlargement of the small open space that remained between the slowly growing amethysts. But at the place where the hanging wall was attached to the footwall, the hanging conglomerate was torn off, and further opening here resulted in the enlargement of a new fissure on the other side of the detached piece. This new fissure

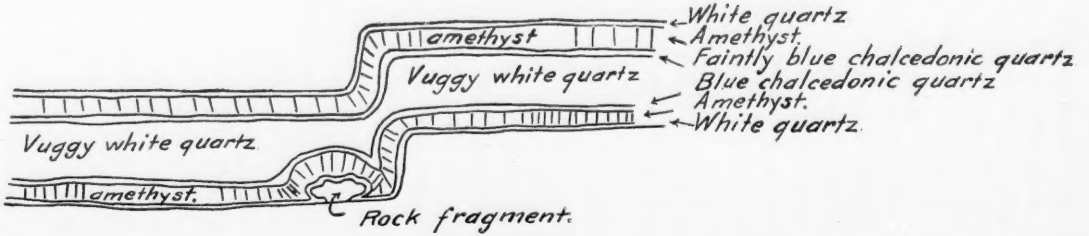

FIG. 1. From Wandke, *op. cit.*, p. 12.

FIG. 2. From Wandke, *op. cit.*, p. 12.

was now filled by blue chalcedonic and later by vuggy quartz. That in Wandke's illustration the amethyst band on the other wall is not interrupted may be understood, if we assume that the spot where the piece of conglomerate was torn off lies out of the plane of the picture. Otherwise the existence of three bands of amethyst, *i.e.*, on the upper wall, on the footwall, and beneath the piece of conglomerate, cannot be explained.

In Fig. 3 (Wandke's Fig. 6) I see a part of the vein where the fissure was locally enlarged further during the formation of vuggy quartz. The fissure was in great part firmly closed by the first steps of the crystallization of vuggy quartz when at the spot illustrated by Wandke, a new movement tore away a part of the hanging wall and gave room for a new deposit of silica. In the middle of the illustration is a piece of the whole vein showing both series from one side of quartz and carbonate to the other with a middle part of white quartz lying unsupported in the vuggy quartz. The other fragments are from parts of the vein where there existed still some open spaces not yet closed by the first white quartz. They consist, therefore, of only one series (quartz and carbonate, silver sulphide, amethyst) from the hanging wall.

Above I have particularly mentioned lodes in which the opening of fissures was faster than their filling by crystallization. The opposite is much more common. A little fissure is opened, filled and firmly closed by the oldest crystallization products. The tension in the rock re-accumulates; another fissure is opened, cutting the first veinlet (see Fig. 3 in Wandke's paper). If the content of the solutions has changed in the meantime, the second vein is filled by other material. Commonly the new cracks open amidst the old. Where the rock is firmer than the vein material, a symmetrical structure is to be seen in part of the veins. The inner part of some veinlets is different in composition and younger than the outer part, but the younger mineral does not hold strictly the middle of the vein; in places it runs on one side and abruptly leaves the old vein, forming a parallel veinlet. As a rule, if the velocity of vein-filling is greater than the velocity of fissure-opening, a complicated system of veinlets results, and all the pieces of rock between such veinlets are "unsupported fragments."

FIG. 3. From Wandke, *op. cit.*, p. 13.

Cracks tend to be opened at the weakest part of the rock-vein-system. If the fissure is accompanied by a slickenside or by gouge, these tend to be the weakest point of the system. Then, the first crack opens along the gouge and is immediately filled by the first crystallization product. New movement opens a new crack between the gouge and the first crystallization; new minerals therefore follow and adjoin the first. A non-symmetrical banded structure is the consequence of this process, in places suggesting even a sedimentary origin for the deposit where the fissure runs comformably to the layers of the wall rock. In Carinthia I have seen wonderful proofs of such accretion of quartz layers in large, low grade, gold-quartz lodes.

It is unnecessary to say that the relative velocities of the mechanical and the chemical process, of the opening and the filling, may vary several times. A broad symmetrical banded lode may be penetrated by small cracks of younger mineralization or, in a zone of complicated veinlets a banded lode of younger material may open. This case is rare since the existence of veinlets and cracks ordinarily prevents the formation of a straight open fissure in the rock-vein system.

SUMMARY.

In many papers on ore deposits are statements that the opening of fissures and their filling by vein material have not been successive processes, but that the fissures and cracks continued to open during the crystallization of the vein material. The author offers the hypothesis that this is the rule in the formation of nearly all veins and that the vein structure depends mainly on whether the opening was faster or slower than the filling. In the first case the minerals are laid down in symmetrical layers but the open space at any time could not have been much broader than the last layers deposited on the walls. In the second case any crack was immediately closed by vein material and the tension that opened the fissure formed new cracks following paths more or less different from the original fissure. Many problems that have

suggested different periods of mineralization, magmation, solution pressure, pressure of growing crystals, shrinkage produced by the passage of pre-ore solutions, sometimes even replacement and, especially, the problem of " unsupported fragments " may readily be explained by the hypothesis of vein-filling during opening.

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DISCUSSION

CRITERIA OF AGE RELATIONS OF MINERALS.

Sir: In the September–October issue of this journal the authors of the paper on Criteria of Age Relations of Minerals[1] state (p. 603):

> "Obviously the pyrite has developed by the simultaneous replacement of the several minerals of the schist. A further implication not generally recognized is that the several minerals of the schist must have been replaced at essentially the same rate, a somewhat astonishing fact in view of the diverse solubilities of these several minerals under most circumstances."

Now it is my belief that on the assumption of certain reasonable conditions the obscurity attending the phenomenon can be cleared up. Let us abstract the following conditions:

1. A growing pyrite crystal.
2. A gangue of alternate laminae of relatively insoluble and soluble minerals.
3. A mineralized solution circulating so slowly that for the moment it may be regarded as stagnant.

It follows from the necessities of the case that an open space of capillary width must separate the pyrite face from the gangue as, otherwise, circulation of the solution would not be possible. Furthermore, in order that metasomatic action may take place at all, it is evident that the solution must be supersaturated in respect to the FeS_2 molecule and it must have the power of dissolving the gangue minerals, each in the degree of its solubility, only after it has deposited its burden of iron sulphide on the crystal face. According to the law of mass action the precipitation of iron and the solution of gangue proceed *pari passu*. Moreover, to satisfy structural requirements, crystal growth advances by successive

[1] Bastin, E. S. et al: ECON. GEOL., vol. 26, pp. 561–610.

increments of one molecule thickness deposited evenly over each face.

Fig. 1 represents a situation where a soluble gangue mineral has been attacked more intensely than its relatively insoluble neighbors, and fresh solution is supposed to occupy the open spaces in front of the pyrite crystal face. The solution now precipitates a film of FeS_2 on the pyrite face, thereby disturbing the homogeneity of the solution; for, owing to the lesser volume of the

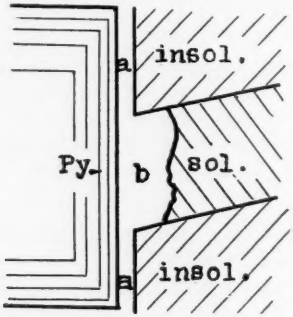

FIG. 1. Condition favoring solution of less soluble gangue minerals in preference to those more soluble.

liquid, the concentration of the FeS_2 molecule has been reduced at *a–a* more than at *b*. Therefore the solvent power of the solution at *a–a* is more active than at *b;* the solution will selectively attack the less soluble mineral until volumes and concentrations have established equilibrium, when diffusion ends the cycle and the introduction of fresh solution starts a new one.

The contention that pressure of the growing pyrite crystal would act selectively on a relatively insoluble gangue mineral to increase its solubility would seem to be invalid for the reason that such pressure would close the channel and so arrest all chemical action, whereas the explanation proposed here assures circulation so long as the solution satisfies the physico-chemical conditions necessary for replacement.

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REVIEWS

Lehrbuch der Erzmikroskopie, Volume II. By HANS SCHNEIDERHÖHN AND PAUL RAMDOHR. Pp. 714, figs. 235. Gebrüder Borntraeger, Berlin, 1931. Price (bound), 72 marks.

This book is the second volume of a set of two. The first volume has been promised us for 1932. A small volume of determinative tables for use with the second descriptive volume has just come off the press. The whole work is supposed to be the second edition of H. Schneiderhöhn's "Anleitung zur mikroskopischen Bestimmung und Untersuchung von Erzen und Aufbereitungsprodukten besonders im auffallenden Licht" (Berlin, 1922), but the 130 pages of the descriptive part of the old edition have grown to the 640 pages of the new volume. According to the preface the major part of this volume is from the pen of Dr. Ramdohr. Almost all opaque and many semi-opaque minerals have been described in great detail. Only a few of the very rare minerals have been omitted. Order and space allotted to the minerals are as follows: 15 elements, 57 pages; 67 sulphides, 254 pages; 67 sulphosalts, 168 pages; 32 oxides, 119 pages; 17 gangue minerals and non-opaque ores, 23 pages. Under each mineral name are given: (1) Chemical formula, crystallographic and certain physical constants; (2) the behavior when being polished and the hardness; (3) color, intensity and kind of reflection of polished surface; (4) etch tests; (5) textures and structures, twinning, zoning, grain size, replacement, etc; (6) possible confusion with other minerals; (7) geological occurrences, paragenesis and origin; (8) localities of specimens examined; (9) literature.

The authors adhere to this classification strictly, a fact which makes this volume a very fine reference work not only for economic geologists and mineralogists, but also for crystallographers and metallurgists. The illustrations are most excellent and well chosen. All of them originated in the authors' laboratories with the coöperation of assistants, students and preparators. Two complete alphabetical indexes of minerals and localities add greatly to the usefulness of this book. The authors are to be congratulated on the thoroughness and high standard of scholarship displayed throughout the work. It is to be regretted, however, that the price of the volume is so high. It seems that the printed matter could have been condensed a great deal and yet not have lost any its distinctness and legibility, which are practically flawless.

The criteria for mineral determination which are stressed are chiefly optical as distinct from chemical ones which have been used for so long. Schneiderhöhn and Ramdohr think that chemical tests on polished surfaces are too often misleading especially where two or more minerals are closely associated. This, it would seem, would also be the case with light intensity and color measurements with the photometer ocular and the photo-electric cell to which considerable space is devoted under each mineral. Chemical tests are cited mostly from Murdoch and Davy and Farnham. They distinguish these tests carefully from those reactions that produce so-called "structure etching" of which Schneiderhöhn claims to have been the originator in 1921 (page 8).[1]

To some investigators the use of the low power oil immersion objectives will be new. Schneiderhöhn and Ramdohr give color comparisons of polished surfaces in oil and in air for each mineral. The data on pleochroism in reflected polarized light (only the polarizing nicol is used) will be welcomed by American investigators, who apparently have not made full use of this method. Information on the behavior between crossed nicols is also given. The paragraphs on textures and structures are veritable gold mines of information and show the thoroughness with which the authors have gone over the literature and supplied data of their own.

Economic geologists will be greatly interested in the parts dealing with replacements, paragenesis and origin of the minerals. It seems to the reviewer that many statements here by Schniderhöhn and Ramdohr are too positive and based on personal opinion rather than proof. Not infrequently one reads a sentence to the effect that a statement by a certain investigator is "wrong" (falsch), or that it is "sure" (sicher). One wonders how things can be so "sure" or "wrong" in this branch of geology and mineralogy. The authors have tried to acknewledge their sources of information in a large bibliogrphy of 618 references. At the same time they have jealously guarded their own contributions, which accounts for the occurrence of their own names more often than is usual in a text book. (On 40 random pages their names are found in 41 places.)

The order in which references are given in the text for each mineral seems to be mostly a matter of convenience. This leads to situations which give one the impression that the work done in the authors' laboratories far exceeds in importance that of other workers in the same field. As a matter of fact one may read on the first page of the preface that

[1] This is evidently an error on his part, for some years previously several Americans had systematically used this method on ore minerals. See for example, Tolman, C. F., Am. Inst. Min. Eng., 1916, pp. 402–433, a reference also contained in the reviewed volume.

the two authors have collected more microscopic material and have studied more polished sections than is probably the case anywhere else.

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UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

Bulgarische Kohle: Beiträge zur Kenntnis ihrer Geologie und Wirtschaft. By E. HABERFELNER AND H. MÜLLER. Pp. vi+132, figs. 75, maps 5. Ferd. Enke, Stuttgart, 1931. Price, 18 Rm.

This, the eighth publication in the Brennstoff-Geologie series, edited by Dr. Stutzer, is divisible into two parts. The first, by Müller, deals with the coal industry of Bulgaria, describing the occurrence of the coal beds and of the mines, their production, and the costs and selling prices of their products. The total production of the country is about 1,500,000 tons, an amount which might be greatly increased if there were sufficient demand. At present, the household use of coal is only about half of that of wood; consequently it is believed that if the householder could be persuaded to substitute the more convenient fuel for the less convenient one, a market might be made for 500,000 to 800,000 tons of coal. The authors estimate that other outlets might increase the total production to 3,000,000 tons annually, and that at this rate the reserves would last 600 years.

In Haberfelner's discussion a brief description of the stratigraphy and the complicated tectonics of the country is given, with a little fuller account of the coal-bearing formations. Anthracite occurs in the Upper Carboniferous and in the Jurassic in complexly folded and faulted rocks, but it contributes less than 6 per cent. to the nation's coal output. The principal production comes from the Lower and Upper Miocene, which are less complexly folded than the older beds. This coal is mainly lignite (Braun Kohle), containing about 4 per cent. S, 7–19 per cent. ash, 14–27 per cent H_2O, and 33–43 per cent. volatiles, and having a thermal value between 2900 and 5000.

W. S. BAYLEY.

The Climax Molybdenum Deposit of Colorado. By B. S. BUTLER AND JOHN W. VANDERWILT. With section on History, Production, Metallurgy and Development, by CHARLES W. HENDERSON. Colorado Scientific Society Proceedings, Vol. 12, No. 10, pp. 309–353, 1931.

The Colorado studies of ore deposits, directed for the past five years by Dr. Butler, under Federal-State coöperation, were urged by the decline of a great metal region, and the need for new ore there which does not outcrop. They involve field work in large amount, and are prophetic of a time when we shall have continuous public record of every mining

operation. This paper summarizes one of these studies, in advance of fuller publication.

The subject of the paper was known 20 years ago as a mile-wide rusty blot on a desolate highland of 12,000 feet altitude, close to glacial cirques and permanent snowbanks. Here and there, a hole beaten out by the prospector revealed stains of yellow oxide and specks of shining sulphide. Today the ground below this blot, with fractional development, shows 50,000,000 tons of 0.5 per cent. molybdenum, provides all but an eighth of the molybdenum used in the world, and through its assured reserve, is a reason for the acceptance of molybdenum as a standard alloy metal. Its owners have welcomed geologists, and this study has been made under the direction of one of our most thoughtful, experienced and original field scholars.

The ore body, 1500 feet by 3000 feet in area, lies symmetrically within the rusty blot above mentioned. It contains a core of quartz, 700 by 1000 feet. Underground development shows the ore and its core to enlarge downward like truncated, nested domes. The ore resembles "disseminated copper"; we have only to decrease the molybdenite and increase the chalcopyrite and we have the ore of Bingham. In shape, it is like Bingham, formalized and furnished with a quartz core of more intense alteration. In reality, it is a great pegmatite pipe replacing, in Tertiary (?) time, pre-Cambrian granite and schist and, like the Colorada pipe of Cananea, affording a linkage between the pegmatite pipe and the disseminated copper deposit.

The treatment by Messrs. Butler, Vanderwilt and Henderson shows strongly against the background of methods commonly followed in geological writing. These are of two kinds: (1) The catalog of facts, without projection in place or time, or regard for process: illustrated by descriptive mineralogy. (2) The coördination into plausible wholes: involving dramatic emphasis and suppression of the alternative; involving the personal "view," the "school of belief."

The Climax paper seems at first glance to be of the first kind. It yields a plain, condensed description and, although the senior writer is a pioneer in ideas of process, he at no point allows his speculations to distort the record. The reader feels that, should he himself study this ground carefully enough, he would see in it these same particulars. There is no trimming to a previous pattern of idea. Nevertheless, the paper has a large ingredient of the second kind. It is not a mere catalog. In spite of the realism of its materials and their radical heterogeneity, it composes into logical form. In other words, it is a restrained presentation of facts picked out in accordance with a rich and varied previous experience. It employs a cautious, wise selection sufficient to create a vivid geological picture.

The nature of the selection and restraint is revealed if we examine the considerations which were omitted. These are divisible into the groups, *source, travel* and *precipitation.*

First as to *source.* Whence the "mineralizing agents"—the copper and molybdenum, the energy and the fluids, including water, which flooded this ground in multiple volume compared with the materials which we now see?

Disseminated copper ore bodies lie in or near igneous "stocks" (lately found, in a number of deep developments, to be sheets, wedges, lenses). By custom, the "stock" has been called the "source." But, lately, several of the "stocks" have been found to be cut by later, pre-ore porphyries with quartz phenocrysts, in prongs and dikes following cracks similar to or identical with those followed by ore. This has interposed a drastic time-space between the "stock" intrusion and the ore and has weakened and blurred the idea of source.

The Climax ore body is similarly related to a stock. But this stock, pre-Cambrian granite, is cut by Tertiary (?) pre-ore dikes of monozonite porphyry with conspicuous quartz phenocrysts.

In the Climax example, the time interval, exceeding five hundred million years, between the stock and the ore, is an impressive warning against source deductions without independent proof of time relation. Evidently the authors so regard it. Even concerning the dikes which approach nearer in time to the ore, they say, ". . . their association with the ore is not sufficiently close to point to them as sources of mineralization."

But, in any event, what do we mean by source? Were all these materials and the energy involved with them, emitted from a single place? Have we a connection here with an "original, igneous hearth," 50 kilometers deep? Or, instead, is it a connection with a "magma pocket" close at hand? And, in either case, what part is played by the dikes?

Moreover, if some such connection exists, and if the magma exercises a function, what kind of a function is it? Was this magma originally peculiarly rich in these constituents? Or, was it an average magma, on its way toward the surface and in some way so conditioned as to yield these products at this time and place.

Or, to go to another extreme, was it merely a heat function, as in the exhalation of hot carbon dioxide gas, the molybdenum, copper, sulphur, fluorine, iron, silica, etc., being provided through the alteration of rocks, and the H_2O being groundwater?

Evidently, of this function, so hidden in alternatives, the thought of the geologist and of the physicist, even in its most austere form, tells us little. Whatever the "view" taken, study opens another view of quite a different kind, and no less acceptable. Assuredly, the view in general

that, because ore coincides in place with an igneous rock, and seems to have travelled along the same path, the rock is therefore its "source" in some particular, selected way, is unreasonable. We can use the source-relation only in a broad sense within which we do nothing but set up a number of alternatives.

Next, as to *travel*. Whatever their source, how did these materials travel to this place? This ought to be more tangible than the question of source, for some of its evidence is nearer at hand. Unfortunately, all we know at Climax is that, while the ore is elongated along the Mosquito Fault, and while many dikes parallel the fault, both ore and dikes antedate most and perhaps all of the fault movement. No structural peculiarity has been found which, were the ore covered up, would specify this mile of fault as more favorable than one of the many other miles. There is no especial abundance of dikes here, for example. The strongest suggestion of structural pecularity is the stock of pre-Cambrian granite which, though sprawling, with arms stretched along the fault, still symmetrically contains the blot of iron-stained rock much as that blot contains the ore. An alternative here is that the granite stock has a source-function which is mechanical only; being a strong rock, it carried cracks deep below the zone of flowage for weaker adjacent rock. As to whether the channel was made on an old zone of faulting recurrent through geologic ages, or whether it belonged to a single episode, we do not know.

Our inferences, even as to travel, are not, then, very specific. All we are sure of is the general conception that, starting from an unknown source, the ore-making fluid followed, with declining pressure, a continuous channel for an unknown distance into the ground where mining is now in progress; and in passing through this ground it must have been on its way to the surface. The nature of that fluid at various stages of its journey is full of possibility. Did it start out with molybdenum? If not, did it pick the molybdenum up on the way, as, for example, in the alteration of the granite to what is now the silica core? Furthermore, did the molybdenum travel in an acid fluid (rich in chlorine or fluorine)? What was the density of the fluid? What is the molybdenum, fluorine and chlorine content of the fresh granite? Of the fresh dike rock?

What was the temperature? Evidently the fluid was, not "cold," but "thermal." Was the channel enveloped by a hot layer permitting only slow conduction, and delivering the fluid, at the place where ore now is, only slightly cooled below the temperature of the source? Does the channel carry an early deposit correlated with the more rapid heat loss during the creation of the envelope? Or, was such an early deposit re-dissolved as the temperature rose again?

Lastly we come to *precipitation*. Here, if anywhere, we should be able to know, for precipitation is the process whose place we see.

The first question is: why, in the upward course of the channel, this sudden burst of minerals? It coincides with a multiplication of the openings. At this very place, the channel has split into millions of parts. The Climax mineralized body is "crackled" throughout. Instead of heating the walls of a compact canal, the fluid was here divided into tiny diverging streamlets and was made to heat and to alter throughout, a cubic mile of ground, cooled, as seems likely, by circulating ground-water. The heat loss was large and rapid. Was this heat loss, with the accompanying pressure drop, the principal change of condition and localizer of this mineral node? And was this a place for the boiling and separation of volatiles, and for a residual solution of new composition to percolate through the rock? Were the heat changes here occurring so radical, so quickly effected, so uncorrelated with source conditions and so governed by conditions at the terminus, as to impair the significance of classification of this ore by temperature?

But, how was the channel split? Why was the rock cracked in this peculiar, thorough manner? Had this granite stock some "coiled-spring" stress, residual from its freezing and deep burial? Can we devise a means of measuring such stress? Or, did alteration and shrinkage cause breakage and upward and outward growth of cracks so long as the fluids continued to pass? Is local subsidence visible in the structure?

Further, why was the channel split at this especial place in vertical section? Is it that we are here near the top of the granite where the fluids are about to sill out under quartzite?

Finally, what was the upward (now eroded) terminus of the ore and what is the downward terminus (not yet reached)? The vertical section shows walls contracting upward; a natural but not necessary inference is doming a few hundred feet above the present surface. As to depth, analogy suggests that the walls will soon straighten, and finally draw together in one or more roots.

These problems, in their present state, we should thank Dr. Butler and his co-workers for dismissing energetically from the paper. Together with Dr. Knopf and a few other recent writers, these authors resist the time-honored vogue of ideation in ore geology, and show the value of a new, and more penetrating, descriptive treatment.

AUGUSTUS LOCKE.

Principles of Structural Geology. By C. M. NEVIN. Pp. 303, figs. 126. John Wiley & Sons, New York, 1931. Price, $3.50.

This appears to be the best text book on structural geology that has yet been produced. It is well written, excellently illustrated, and the subject is presented in a manner to stimulate the student's interest. Con-

troversial problems are not avoided and well chosen references lead the student to different view-points.

The chapter headings give an idea of the contents. They are: I, Physical Properties of Rocks; II, Stress and Strain Relations; III, Flexures; IV, Faults; V, Joints; VI, Cleavage; VII, Structures in Unconsolidated Sediments; VIII, Reflection of Rock Structures in the Topography; IX, Facts, Inferences, and Hypotheses regarding the Earth; X, Continents and Ocean Basins; XI, Mountain Systems.

The volume is brought out in the usual fine form of Wiley books, with good paper and typography. It is well adapted for a classroom text and should be in the hands of all geologists and mining engineers.

ALAN BATEMAN.

Oil and Sulphur Development in the Texas and Louisiana Gulf Coast Salt Dome Region. Bull. No. 1 of the Texas Gulf Coast Oil Scouts Association and South Louisiana Oil Scouts Association, 1930. Pp. 128; maps, sections and tables. Houston, 1931.

This valuable compilation of data on the Gulf Coast consists of a series of mostly anonymous brief articles on: the history of the known domes and oil fields, production and development statistics, pipe line outlets and capacities, available storage capacities, lease forms and geophysical permits, geology and geophysics in and of the Gulf Coast, sulphur, well surveying in the Gulf Coast, Clay Creek, Barbers Hill, Raccoon Bend, Sugarland, Old Hackberry, and East Hackberry domes. Many valuable and easily consulted statistical tables are given. Original data have been released in many of the articles and tables, and many facts are easily available here which it would be tedious to assemble. The article, "The Geology of the Gulf Coast Area of Texas and Louisiana," is by far the best discussion available in the literature of the Gulf Coast stratigraphy. This bulletin probably contains more data but less theory on the salt domes and the Gulf Coast than the A. A. P. G. salt dome volume. The reviewer recommends the acquisition of this bulletin by all geologists and geological libraries which are interested in the Gulf Coast.

DONALD C. BARTON.

Copies of books mentioned under "Reviews" or under our "New Book List" (see advertisement page) may be purchased through our Journal Bookshop by writing to W. S. Bayley, University of Illinois, Urbana, Ill.

BOOKS RECEIVED.

By

D. GALLAGHER.

Carte Géologique du Katanga. By M. ROBERT. Pp. 13, map. Publication du Comité Special du Katanga, Bruxelles, 1931. Geologic map of southern Belgian Congo from 4° 60–S to 13° 30–S and 23° 60–E to 31° –E. 32″ x 40″, scale one to one million, in full color, with explanation.

The Tertiary Mollusca of the Gisborne District (New Zealand). By J. MARWICK. Pp. 177, pls. 18. N. Z. Geol. Surv. Paleontol. Bull. 13, Wellington, 1931, 13/9.

Surface Water Supply of the United States, Water Supply Papers, U. S. Geol. Survey. Gaging-station records. *1927, Part II,* W. S. P. 642. *1927, Part XI,* W. S. P. 651. *1927, Part XII,* W. S. P. 652, 653, 654. *1928, Part I,* W. S. P. 661. *1928, Parts IV–XII,* W. S. P. 664–674 incl. *1929, Part XI,* W. S. P. 691.

Origin and Microfossils of the Oil Shales of the Green River Formation of Colorado and Utah, by W. H. BRADLEY. Pp. 58; pls. 28; figs. 3. U. S. Geol. Surv. Prof. Paper 168. Washington, 1931. 60 cts.

Gold Coast Colony Geological Survey Report for 1930–31, by N. R. JUNNER ET AL. Pp. 17. Accra, Gold Coast, 1931. Accounting of work done for the year.

Geology and Ore Deposits of the Goodsprings Quadrangle, Nevada, by D. F. HEWETT. Pp. 172; pls. 40; maps; figs. 55. U. S. Geol. Surv. Prof. Paper 162. Washington, 1931. $1.15.

The section on rock alteration is one of the most outstanding portions of this excellent paper, and is a valuable contribution to the problem of dolomitization.

Agglutinating, Coking, and By-product Tests of Coals from Pierce County, Washington, by S. M. MARSHALL AND B. M. BIRD. Pp. 31, figs. 13. U. S. Bureau of Mines, Bull. 336. Washington, 1931. 10 cts.

Relationship Between Volatility and Consumption of Lubricating Oils in Internal-combustion Engines, by G. WADE AND A. L. FOSTER. Pp. 52, figs. 7. U. S. Bureau of Mines, Tech. Paper 500. Washington, 1931. 10 cts.

Need for Conservation and Protection of Our Water Supply with Special Reference to Waters from the Ocala Limestone, by H. GUNTER AND G. M. PONTON. Pp. 15, maps, figs. Florida State Geol. Survey, 21st–22d Annual Rept., 1931.

The Possibility of Petroleum in Florida, by H. GUNTER AND G. M. PONTON. Pp. 7. Florida State Geol. Survey, 21st–22d Annual Rept., 1931.

Typical Rocks and Minerals in Illinois, by G. E. EKBLAW AND D. L. CARROL. Pp. 79, figs. 41. Illinois Geol. Surv. Educ. Ser. 3. Urbana, 1931. Brief and elementary treatment, to meet the demands of the public schools.

Nova Scotia, Canada, by H. S. PHILPOT. Pp. 157, illus. National Devel. Bureau, Dept. of the Interior, Ottawa. 4th ed., 1930. Descriptive guide book to the Province.

Geology and Mineral Resources of the Cleveland District, Ohio, by H. P. CUSHING, F. LEVERETT, AND F. R. VAN HORN. Pp. 138, pls. 23, figs. 11. U. S. Geol. Surv. Bull. 818. Washington, 1931. 65 cts. General geology, stratigraphy, geologic history with special attention to glacial lakes, economic geology. Two large, full color maps of bed rock geology and Pleistocene geology.

Geology of the North-Eastern Pretoria District, by B. V. LOMBAARD. Pp. 43, figs., map in color. Union of South Africa Geol. Surv. Sheet Map No. 18 (Moos River). Pretoria, 1931. An explanation of sheet map No. 18.

Investigations in Ceramics and Road Materials, 1928–1929, by H. FRÉCHETTE ET AL. Pp. 134. Canadian Dept. of Mines, Mines Branch 722. Ottawa, 1931. Ten papers by various authors.

Engineering Report of Cotton Valley Field, Webster Parish, La., by J. S. Ross. Pp. 69, figs. 23. U. S. Bureau of Mines, Tech. Paper 504. Washington, 1931. Geology, oil production, and production methods, with production of the field.

The Geology of the Country around Shamva, Mazoe District (Southern Rhodesia), by R. TYNDALE-BISCOE. Pp. 87, pls. 12, figs. 6, geologic map in color. Southern Rhodesia Geol. Surv. Bull. 18. Salisbury, 1931. Price, 3/9. General geology, stratigraphy, petrography, gold mines, rock analyses.

Results of Electrical Resistivity and Electrical Induction Measurements at Abana Mines, Quebec, Canada, by E. V. POTTER. With Explanation of Some Factors Associated with Induction Method, by F. W. Lee. Pp. 28, figs. 22. U. S. Bureau of Mines, Tech. Paper 501. Washington, 1931. 15 cts.

A Selected List of Books and References on Geophysical Prospecting, by C. A. HEILAND AND D. WANTLAND. Pp. 24. Colo. Sch. of Mines Quar., vol. XXVI, No. 3. Golden, Colo., July, 1931. 50 cts. Lists about 200 papers, mostly of recent publication.

Les Annales du Service des Mines du Comité Spécial du Katanga, Tome I, 1930. Pp. 68. Bruxelles, 1930. 30 francs. Contains: Contribution à l'Etude Géologique des Bassins Houillers de la Luéna, by R. Cambier (pp. 53, pls. 10, map in color), and four short papers by other authors.

The Adventure of Mankind. By EUGEN GEORG. Translated from the German by R. BEK-GRAU. Pp. 325. E. P. Dutton & Co., New York,

1931. Price, $5.00. A story of the birth of culture, based on a geological background of the latter phases of the formation of the Earth's surface; involving the hypothesis of Atlantis, and leading to an interesting philosophy of man and his environment and development. Interesting reading.

A Preliminary Report on the Artesian Water Supply of Memphis, Tenn. By F. G. WELLS. Pp. 34, map. U. S. Geol. Surv. Water Supply Paper 638–A, Washington, 1931.

Geology and Water Resources of the Middle Deschutes River Basin, Oregon. By H. T. STEARNS. Pp. 95, map. U. S. Geol. Surv. Water Supply Paper 637–D, Washington, 1931. General geology, geology of dam sites, and water resources of the region.

Influence of Fractionation on Distribution of Sulphur in Gasoline, by R. H. ESPACH AND H. P. RUE. Pp. 24, figs. 11. U. S. Bur. of Mines, Tech. Paper 505. Washington, 1931. 10 cts.

Geological Survey Affairs (Kentucky), by W. R. JILLSON. Pp. 375. figs. 140. Kentucky Geol. Surv., Ser. VI, vol. 35. Frankfort, 1930. Ten separate geological papers including two administrative reports.

The Building of Kentucky, by W. H. TWENHOFEL. Pp. 230, figs. 55. Kentucky Geol. Surv., Series VI, vol. 37. Frankfort, 1931. A geologic history. Also contained in the same volume: Mineral Resources of the Ashland, Ky., Region, by W. G. BURROUGHS, 36 pp.; Reconnaissance Survey of the Geology of Northern Hardin County, by A. H. SUTTON, 33 pp.; Reconnaissance Report on Geology of McLean County, by L. C. ROBINSON, 25 pp.

Natural Gas in Western Kentucky, by W. R. JILLSON. Pp. 190, figs. 23. Kentucky Geol. Surv., Ser: VI, vol. 38. Frankfort, 1931.

Oil and Gas in Western Kentucky, by W. R. JILLSON. Pp. 632, illus. 42. Kentucky Geol. Surv., Ser. VI, vol. 39. Frankfort, 1930. Summary statement of drilling and production coupled with the presentation of 494 new well records.

Geological Map of Kentucky, by W. R. JILLSON. In colors, showing geology, mineral resources, structure, and physiography. Scale 1:500,000. Kentucky Geol. Surv., Ser. VI, 1929.

Structural Geological Map of Kentucky, by W. R. JILLSON. Showing all major structural features and their actual elevations, oil and gas pools and pipelines. Scale 1:500,000. Kentucky Geol. Surv., Ser. VI, 1931.

Beryllium and Beryl: Mineral Industry of the British Empire and Foreign Countries. Pp. 26. H. M. Stationery Office, London, 1931. Price, 6d. Distribution of deposits of beryl, its extraction, properties and uses; alloys of the light metal beryllium suitable for aircraft.

Beaches of Florida, by J. H. C. MARTENS. Pp. 52, figs. 11. Florida Geol. Survey, 21st–22d Annual Rept., 1931.

SOCIETY OF ECONOMIC GEOLOGISTS

NEW OFFICERS.

The following officers have been elected in accordance with the new By-Laws of the Society: President for 1932, B. S. Butler; First Vice-President for 1932, Ernest Howe; President for 1933, E. S. Bastin; First Vice-President for 1933, W. S. Bayley.

Regional Vice-Presidents.—Per Geijer, for Europe; L. L. Fermor, for Asia; A. L. Hall, for Africa; J. A. Dresser, for North America; R. M. Overbeck, for South America; E. C. Andrews, for Australia.

Councilors.—Term ends 1932, E. C. Harder, W. O. Hotchkiss, W. T. Thom, Jr. Term ends 1933, F. G. Clapp, G. H. Garrey, G. D. Louderback. Term ends 1934, J. V. Lewis, G. F. Loughlin, E. S. Moore.

ANNUAL MEETING IN NEW YORK, JUNE 1933.

The next Annual Meeting of the Society will be held in New York City immediately before the XVI International Geological Congress. The meetings will be arranged so as to facilitate the attendance of those members from outside of North America who will attend the Congress. The meetings of the Society will immediately precede pre-Congress field trips. Visitors will, as usual, be welcomed to the meetings of the Society.

PROGRAM COMMITTEE.

The Council has endorsed the policy of a continuing Program Committee of three, with one member retiring each year. Additional members may be added to this committee for one year terms. The Program Committee which will arrange the program for the New York meeting is E. S. Moore, James Gilluly, and W. B. Heroy, serving from one to three year terms, respectively.

NOMINATING COMMITTEE.

The following committee has been appointed to nominate officers for the next election: D. F. Hewett, Chairman, W. O. Hotchkiss, W. T. Thom, Jr. As provided in the By-Laws, this committee will nominate one candidate for each office, and this list of nominations will be sent to

all members. After this notice of nominations additional nominations may be made by members, each such additional nomination to be endorsed by ten members. These additional nominations will be added to the final ballot, which will list all final nominees without distinction as to manner of nomination.

ELEVENTH ANNUAL MEETING

The eleventh Annual Meeting of the Society was held at Tulsa, Oklahoma, from December 29th to 31st, 1931, in conjunction with the American Association of Petroleum Geologists and the Geological Society of America and its affiliated societies and the Tulsa Geological Society. This meeting was notable for the wide range of subjects covered by the papers and for the unusual opportunity offered to study the problems of the petroleum industry. Particularly notable were the carefully organized field trips which preceded and followed the technical sessions. The program follows:

Monday, December 28.—Morning. Field trip by train from Tulsa to Oklahoma City Oil Field and return. (With members of G. S. A. and A. A. P. G.) *Evening.* Colloquium on Subsurface Geological Methods (Arranged by A. A. P. G.) Papers by Frederick A. Bush, Fanny C. Edson, L. C. Case and Ira H. Cram.

Tuesday, December 29.—Luncheon of the Society.

Afternoon Technical Session. Business meeting; H. B. Goodrich (Introduced by Sidney Powers)—Early Discoveries of Petroleum in the United States; C. V. Millikan (Introduced by W. T. Thom, Jr.)—Deep Well Drilling Methods; G. C. Branner—Cinnabar Deposits of Southwestern Arkansas; D. F. Kidd (Introduced by Edward Sampson)—Recently Discovered Radium-Bearing Deposits near Great Bear Lake, Canada; Chas. H. Behre, Jr.—The Peripheral Facies on Ore Deposition at Leadville, Colorado; Stirling B. Talmage (Introduced by E. H. Wells)—The Law of Constant Volume; Arthur Notman—Why 6½ Cent Copper?

Evening. Address of Dr. Alfred C. Lane, retiring President of the Geological Society of America, on "Eutopotropism." Smoker and other entertainment. (Crystal Ball Room.)

Wednesday, December 30.—Morning. Joint session with the Geological Society of America and other Societies. Edgar R. Cumings—Address of the retiring President of the Paleontological Society: Reefs or Bioherms?; E. O. Ulrich—Ozarkian and Canadian Sections in North America and the Physical Relations of These Systems to Each Other and to the Cambrian Beneath and the Restricted Ordovician Above; L. C. Graton—Address of the retiring President of the Society of Economic Geologists: The Depth-Zones in Ore Deposition; C. K. Leith—Structural

Patterns in Mississippi Valley Sediments in Their Bearing on the Origin of Lead and Zinc Ores; Alexander H. Phillips—Address of the retiring President of The Mineralogical Society of America: Isomorphous Substitution of Elements in Minerals; William M. Davis—Shorelines of the Santa Monica Mountains, California.

Afternoon. Joint symposium with the A. A. P. G. and other Societies. L. Courtney Decius—Contribution of Petroleum Geologists to General Geology in California; Sidney Powers—Geology of the Northern Mid-Continent Oil District; Fred H. Lahee—Contributions of Petroleum Geology to Pure Geology in the Southern Mid-Continent Area; Marcus A. Hanna—Salt Domes of the United States; J. C. Karcher and Carl A. Heiland—Contributions from Geophysics to Geology; A. W. McCoy—Origin of Local Anticlines in the Mid-Continent.

Evening. Annual Dinner of the Geological Society of America, to which members and guests of the Society of Economic Geologists were invited.

Thursday, December 31.—Morning. J. J. Runner (Introduced by D. H. McLaughlin)—Origin of the Ore-Bearing Cumingtonite Schists (Homestake formation) of the Black Hills, South Dakota; J. Whitney Lewis (A. A. P. G. paper. Introduced by Sidney Powers)—Oil Fields of Cuba; L. B. Snider (Introduced by Sidney Powers)—Copper Deposits at Prague, Oklahoma (with remarks on the mineralogy by Dr. Alfred C. Lane); Henry A. Ley (A. A. P. G. paper. Introduced by W. T. Thom, Jr.)—Gas Resources of the Texas and Oklahoma Panhandles and South-Western Kansas; Edw. Bloesch (Introduced by W. T. Thom, Jr.)—The Dawson Coal Field, Tulsa, Oklahoma; Harry H. Hess (Introduced by Edward Sampson)—Distribution of Ultrabasic Intrusions with Respect to the Appalachians; D. F. Hewett—Manganese Minerals in Sediments; M. M. Leighton—The Extended Research Program of the Illinois Geological Survey.

Field Trips.—The following field trips took place after the meetings. Trip 3. Dec. 30–Jan. 2. Arbuckle Mountains and Ardmore Basin. Structure and Stratigraphy; Trip 4. Jan. 2–4. Ouachita Mountains. Structure and Stratigraphy; Trip 5. Jan. 3–4. Wichita Mountains. Structure and Stratigraphy; Trip 6. Dec. 31–Jan. 1. Little Rock, Arkansas region; newly discovered quicksilver district, Magnet Cove, and the Pike County diamond mines. Especially arranged for Society of Economic Geologist members and guests under the leadership of G. C. Branner.

SCIENTIFIC NOTES AND NEWS

W. C. Mendenhall has been appointed Director of the United States Geological Survey to succeed George Otis Smith, who is now Chairman of the Federal Power Commission.

Per Geijer, after seventeen years with the Geological Survey of Sweden, has accepted a professorship in mineralogy and geology in the Royal Technical University at Stockholm. He will, however, keep in touch with the Survey in research work.

W. H. Collins, Director of the Geological Survey of Canada, delivered in December at Queen's University, Kingston, a series of lectures on the ore deposits in pre-Cambrian rock areas in northwestern Ontario and the geological problems of the original Huronian area.

R. R. Rosenkrans, instructor in mineralogy at Penn. State College, recently discovered native sulphur in Centre County, Pa., according to the statement of Dr. A. P. Honess, professor of mineralogy.

E. T. Mellor has returned to the Rand after spending some time in England.

G. Horn, geologist of the Spitzbergen Office of the Norwegian Geological Survey, is spending three months in a lecture tour in the United States.

W. Kingston, of Victoria, Australia, is in charge of a plan undertaken by the Government whereby unemployed men are assisted by the Geological Survey to obtain an education in prospecting work.

H. G. Turner has recently joined the faculty of the School of Mineral Industries, Penn. State College, as research associate in fuel technology, and will also conduct research work for the Anthracite Institute, of which he is Director of Research, in his laboratory.

H. Reck, formerly in East Africa and now at the Geological Institute and Museum of Natural Science at Berlin, is going on an expedition to East Africa for the British Museum and Cambridge University.

L. J. Pepperberg has resigned as consulting geologist for the Columbia Engineering and Management Corporation and has resumed his consulting practice at Dallas, Texas.

C. F. Williams, of the U. S. Geological Survey, who uses an airplane in his work as mining supervisor at Miami, Okla., finds that the cost per mile exclusive of storage is less than the average cost of the cars used by the Survey, whereas the total cost, including storage and depreciation, compares favorably with that recorded for automobiles.

The National Research Council has announced a Committee on Accessory Minerals of Crystalline Rocks, consisting of E. S. Larsen, J. C. Reed, J. E. Stark, A. C. Tester, A. N. Winchell (chairman), and J. F. Wright.

to study the nature of such minerals, their variation in time and space in igneous bodies and metamorphosed masses, and their distribution in sediments. The committee will attempt to correlate work now in progress and stimulate further study along these lines.

R. A. Daly has been elected President of the Geological Society of America, and N. M. Fenneman, W. E. Wrather, R. S. Bassler, and A. N. Winchell are Vice-Presidents; the Councilors are D. F. Hewett, A. C. Lane, W. J. Meade, W. C. Mendenhall, Sidney Powers, H. Ries, and F. R. Van Horn.

G. M. Schwartz reports that through an oversight on his part Fig. 19, Page 593 of Volume 26, was wrongly credited to him. It was originally used by P. J. Shenon in a thesis presented at the University of Minnesota for the Ph.D. degree.

The next meeting of the Geological Society of America will be held in Boston, in December, 1932.

The Geological Society of America has appoined as an Advisory Committee on policies and projects in connection with the disbursement of the Penrose Fund C. K. Leith (chairman), Isaiah Bowman, Waldemar Lindgren, J. B. Reeside, Jr., R. T. Chamberlin, M. M. Leighton, and F. D. Adams.

The guide books for the next International Geologic Congress, to be held in the early summer of 1933, are being rapidly completed under the able editorship of H. G. Ferguson.

The annual meeting of the Geological Society of America was held at Tulsa, December 28–31. Although there were fewer geologists than usual present from the northeastern section of the country, there were many from the Middle West and Southwest, and it was a large and extremely pleasant meeting. In addition to the regular sessions, the local committee arranged a number of interesting excursions before and after the meetings, and these were largely attended. The local committee are to be congratulated on their excellent arrangements.

J. A. Udden, Director of the Bureau of Economic Geology at the University of Texas, died at Austin on January 5. Professor Udden was connected with the Iowa Survey, 1899–1903, was geologist for the Illinois Survey, 1906–1911, and special agent for the U. S. Geological Survey, 1908–1914. He received an honorary doctor's degree from Bethany College and from Texas Christian University, and was knighted by the King of Sweden in 1911. He was the discoverer of potash in Texas and the first to suggest the probability of finding petroleum on university lands in West Texas.

The recently published 20-volume index (336 pages) of ECONOMIC GEOLOGY for 1905 to 1925, compiled by J. M. Nickles, may be obtained for $3.00 from W. S. Bayley, University of Illinois, Urbana, Ill.